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Sampling and Analysis Research Program at the Paraho Shale Oil Demonstration Plant

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SAMPLING AND ANALYSIS RESEARCH PROGRAM AT THE PARAHO SHALE OIL DEMONSTRATION

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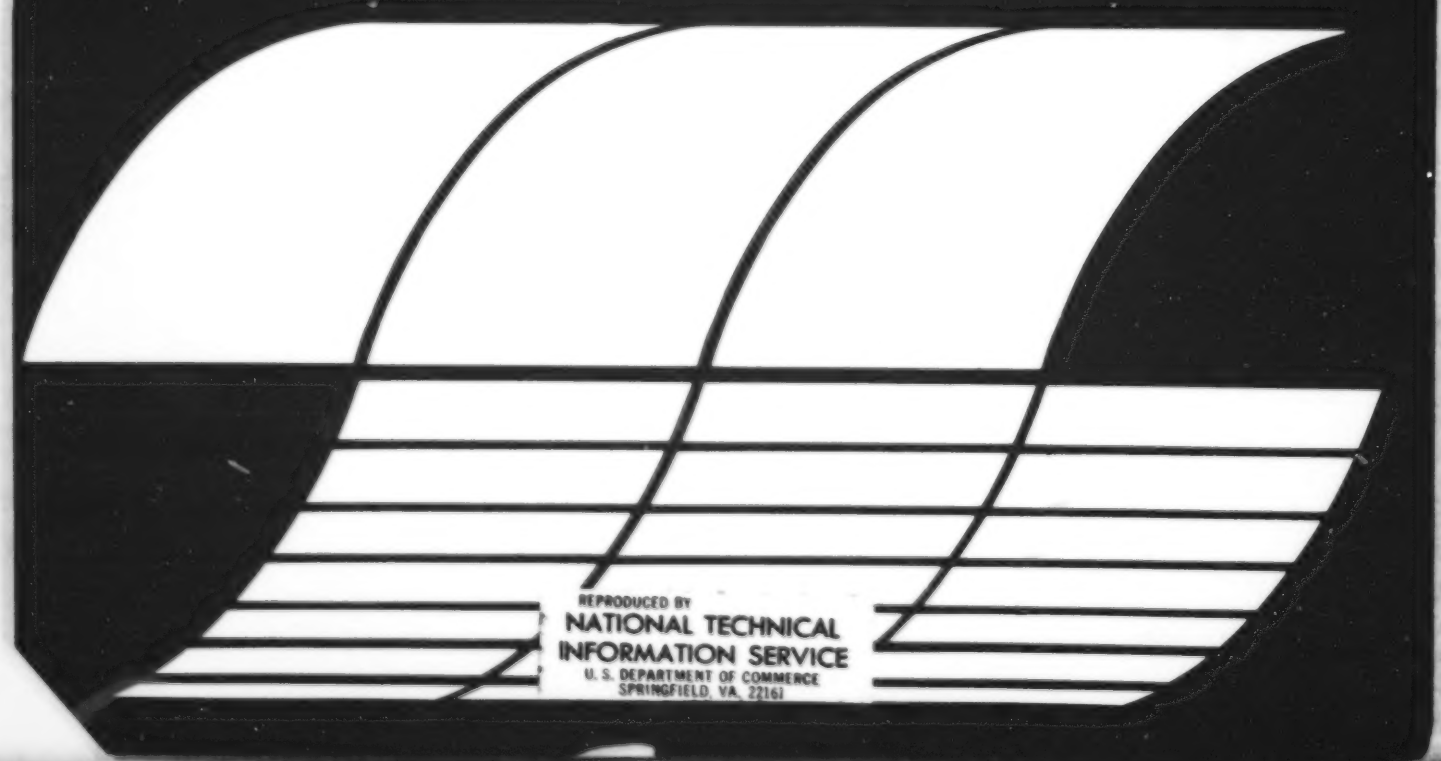
Program Report



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Samples taken included the recycle gases (H_2S, SO_2, NO_x, NH_3, and trace organics), recycle condensate, product oil/water, processed shale discharged from the retorts, and dust in the vicinity of crushing, screening, and conveying equipment. A variety of laboratory analysis methods were used, including wet chemical analysis, spark source mass spectrometry, high pressure liquid chromatography, thin layer chromatography, gel permeation chromatography, and gas chromatography/mass spectrometry methods (GC/MS). Condensate water inorganic analyses were done for calcium, magnesium, sodium and potassium salts, ammonia, gross parameters, and trace elements. Condensate and product water samples were also analyzed for organic neutrals (particularly aromatics), organic acids, and organic bases. Elemental determinations of both retorted shale and raw shale particulates were made.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

New synthetic fuel processes under development need to be characterized prior to commercialization, so that pollution control needs can be identified and control methods can be integrated with process designs. The sampling and analysis research program, conducted at the Paraho shale oil demonstration plant, represents a first step in process characterization. The work reported in this document will serve as a basis for the determination of improved sampling and analysis procedures in future shale oil plant test programs, as well as the selection of testing priorities. Further information on the environmental aspects of shale oil processing can be obtained from the IERL-Cincinnati Fuels Technology Branch.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

A sampling and analysis research program was conducted at the Paraho oil shale retorting demonstration site at Anvil Points, Colorado. The work was carried out by TRW and the Denver Research Institute. The overall objective of the test program was to obtain preliminary quantitative and qualitative measurements of air, water, and solid compositions, and to gain experience that would lead to improved sampling procedures and the determination of priorities for sampling and analysis of shale oil recovery operations.

The existing Anvil Points operations include two vertical retorts: a larger semi-works unit in which a portion of the off-gas was recycled and heated externally to supply heat to the retort and a smaller pilot plant in which air was introduced with recycle gas to support combustion of carbon on retorted shale as a source of process heat. The test plan included both retorts, as their process streams (with the exception of oil product) are essentially different. Selection of sample locations was based on need for information on process streams relative to emissions and effluents expected in a full-scale plant.

Samples taken included the recycle gases (H_2S, SO_2, NO_x, NH_3, and trace organics), recycle condensate, product oil/water, processed shale discharged from the retorts, and dust in the vicinity of crushing, screening, and conveying equipment. A variety of laboratory analysis methods were used, including wet chemical analysis, spark source mass spectrometry, high pressure liquid chromatography, thin layer chromatography, gel permeation chromatography, and gas chromatography/mass spectrometry methods (GC/MS).

Condensate water inorganic analyses were done for calcium, magnesium, sodium and potassium salts, ammonia, gross parameters, and trace elements. Condensate and product water samples were also analyzed for organic neutrals (particularly aromatics), organic acids, and organic bases. Elemental determinations of both retorted shale and raw shale particulates were made.

This report was submitted in partial fulfillment of Contract 68-02-1881 by TRW Environmental Engineering Division under the sponsorship of the U.S. Environmental Protection Agency. This interim report covers the period of June 1, 1975 through December 1, 1976.

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List of Abbreviations and Symbols

Abbreviations

BaP	-- Benzo (a) pyrene
BOD	-- Biochemical oxygen demand
COD	-- Chemical oxygen demand
DEI	-- Development Engineering, Inc.
EDTA	-- Ethylenediamine-Tetracetic-Acid
GC-MS	-- Gas Chromatography and mass spectrometry
GPC	-- Gel permeation chromatography
HPLC	-- High Pressure liquid chromatography
LC	-- Liquid chromatography
K	-- Equilibrium coefficient
meq	-- Milliequivalents
ml	-- Milliliter
mm	-- millimeter
MSA	-- Mine Safety Appliances, Inc.
PAH	-- Polynuclear aromatic hydrocarbons
R_B	-- Relative TLC spot location
SPF	-- Spectrophotofluorometry
SSMS	-- Spark source mass spectrometry
TIC	-- Total inorganic carbon
TLC	-- Thin layer chromatography
TOC	-- Total organic carbon
USBM	-- U.S. Bureau of Mines
µg	-- Micrograms
µm	-- Micron

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The interest and wholehearted support of the Paraho management in the planning and conduct of the test program is gratefully acknowledged. In addition, the involvement and assistance of personnel from the Laramie Energy Research Center (ERDA) has been most helpful in planning the test program, reviewing the data, and coordinating the assembly of data for the final report.

SECTION 1

INTRODUCTION

PROGRAM OBJECTIVES AND UTILITY

Relationship of the Program to Other Work

TRW and the Denver Research Institute are currently performing under contract to the EPA, an environmental assessment of typical shale oil recovery processing. The assessment is particularly oriented towards the evaluation of effluents produced by typical recovery processes, and the appropriate emission control technology and solid waste management techniques.

The TRW contract involves the study of eight oil shale retorting processes that are candidates for commercialization in the near term. To assess oil shale development impacts, the study is designed to establish characteristics which are common to most of the eight processes, rather than to perform an assessment of each individual process. In addition to the preliminary sampling and analysis effort just completed, much longer term testing programs are anticipated at Paraho during 1977 and 1978.

Aims of the Test Program

The Paraho demonstration site is the largest operating surface retort operation going on within the United States (Figure 1). The opportunity to sample and analyze process streams at the site provided an extremely valuable input to the TRW contract. The Paraho Demonstration program, in its current phase, was terminated early in April, 1976, forcing quick execution of the testing program.

The test program was targeted to establish sampling and analysis techniques for obtaining operating data on air and water compositions relative to the crushing, handling, and retorting operations, as well as compositions and quantities related to the retorted shale output of the plant.

The sampling and analysis program at the Paraho site included only those measurements of effluents directly applicable to normal operations of the Paraho process. No ambient air or surface and ground water measurments were made. Because Paraho is an old site (35 years approximately) particular care was exercised to ensure that measurements did not include residual emissions associated with past operations.

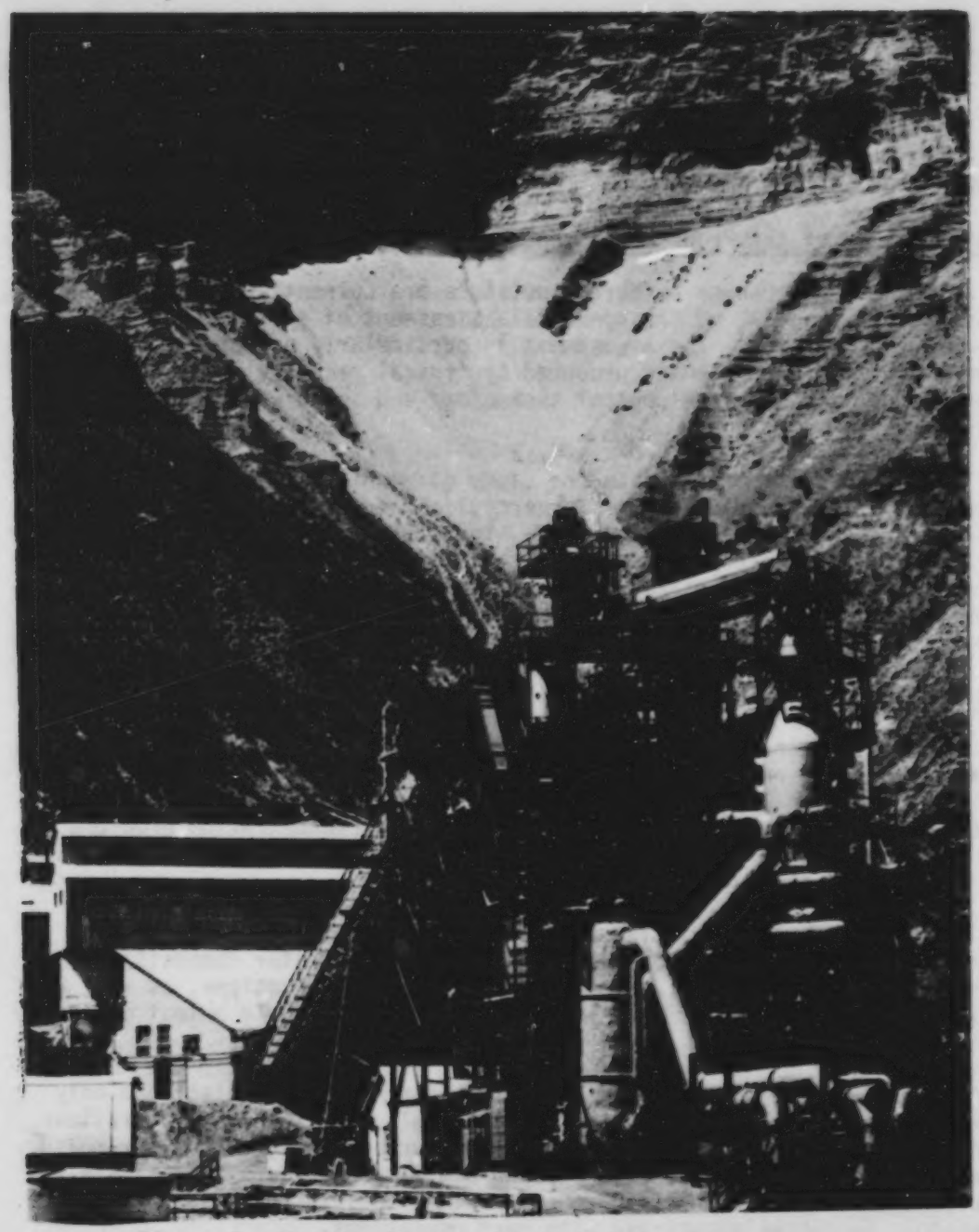

Figure 1. Paraho plant at Anvil Points, Colorado

The actual mining operation was not functional at the time of the test program, precluding emissions testing within the mine and at the mine mouth. Estimates of emissions from mining operations will have to be obtained during future test efforts.

Sponsorship of the Program

The test program was accomplished under contractual arrangements with the EPA, with the concurrent support of the Paraho operating management and personnel from the Laramie Energy Research Center (ERDA). The representatives from these various organizations formed a management team which was responsible for:

- Determination that testing and analysis methods were accepted standard procedures wherever possible
- Verification of Quality Assurance procedures and completeness
- Review of subsequent data analysis, presentation, and interpretation.

Limitations and Uses of the Test Results

The data obtained from the crushing and retorting operations must be considered unique to the Paraho Oil Shale Demonstration. Because much of the equipment and many of the operating procedures used at Anvil Points are not employed in a commercial venture, data pertaining to particulate and dust quantities in the site vicinity cannot be compared to those from full scale Paraho-type operation. A detailed discussion of the Anvil Points equipment and operating procedures is developed more fully in this section.

DESCRIPTION OF THE PARAHO PROCESS AND SITE

The present Paraho oil shale demonstration project utilizes some of the facilities originally developed by the U.S. Bureau of Mines (USBM) at Anvil Points, including an underground room and pillar mine, crushing plant, retort structure, various storage tanks, shale disposal area, and associated laboratories, maintenance shops, and water supplies.

Underground Mining, Crushing

The mine at Anvil Points is a room and pillar operation encompassing the Mahogany Ledge of the Green River Formation, at an altitude of approximately 2440 meters (8000 ft). Mined shale is trucked some 8.8 kilometers (5.5 miles) by road down to the processing area.

At the plant site the mined shale is processed through the primary and secondary circuits of the USBM crushing and screening plant, to produce a feed of approximately minus 7.6 cm (3 in) plus 6 mm (¼ in) size, which is sent to storage bins. The 10-15% fines from the screening plant are stock-piled.

Retorting Plant

Two Paraho-type retorts (Figure 2) have been erected in a steel structure, adjacent to the old USBM gas combustion unit. These include a 1.4 meters (4.5 ft) O.D. (2.5 ft I.D.) by 18 meters (60 ft) high pilot plant unit; and a semi-works retort which is 3.2 meters (10.5 ft) O.D. (8.5 ft I.D.) by 23 meters (75 ft) high. The old USBM gas combustion unit has been converted to a thermal oxidizer for retort off-gas incineration.

Provision has been made for operating the retorts in either the direct mode or indirect mode. In the direct mode (Figure 3) the carbon on the retorted shale is burned in the combustion zone to provide the principal fuel for the process. Low calorie retort gases are recycled to both the combustion zone and the gas preheating zone.

In the indirect mode (Figure 4) heat for retorting is supplied by recycling off-gases through an external furnace, thus eliminating combustion in the retort and producing a high heating value, 8000 kcal/std cu meter (900 BTu/SCF) off-gas.

In either mode of operation, raw shale is fed into the top of a Paraho retort and passed downward by gravity successively through a mist formation and preheating zone, a retorting zone, either a combustion zone (direct mode) or heating z ne (indirect mode), and finally, a residue cooling and gas preheating zone. It is discharged through a hydraulically-operated grate, which controls the throughput rate and maintains even flow across the retort. This grate, the feed mechanism, and the multi-levels of heat input, are among the unique contributions of Paraho technolcgy toward improving the retorting principle in vertical kiln type retorts.

The retorted shale is discharged from the retort at about 150°C (300°F), essentially unchanged from its feed size-distribution, and sent to the shale disposal area originally developed by the Bureau of Mines.

The shale vapors produced in the retorting zone are cooled to a stable mist by the incoming raw shale (which is thereby preheated), and leave the retort. This mist is sent to a condenser, and finally a wet electrostatic precipitator, for oil separation. The resulting shale oil is transported to storage. A detailed description of the Paraho process is given in another report.*

Plant Conditions During Field Test Program

There has been considerable mining and pilot plant activity at this location over the past 35 years, initially by the Bureau of Mines and later by a petroleum company consortium. Much of the auxiliary equipment used by Paraho

*Technological Overview Reports for Eight Shale Oil Recovery Processes, USEPA/IERL, Cincinnati, Ohio (December 1976).

*from Jones, John B., "The Paraho Oil Shale Retort, 81st Nat. Mtg., AIChE, Kansas City, Mo., April 11-14, 1976.

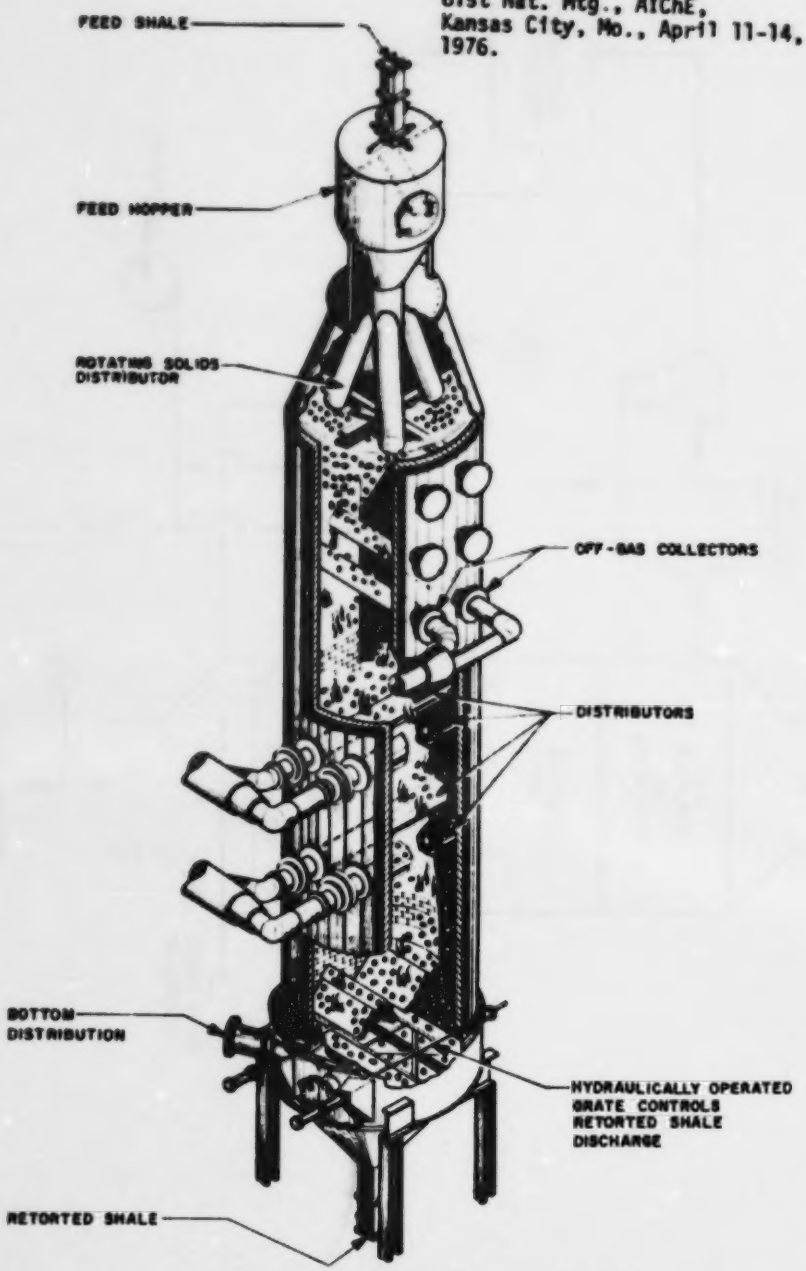

Figure 2. The Paraho retort.

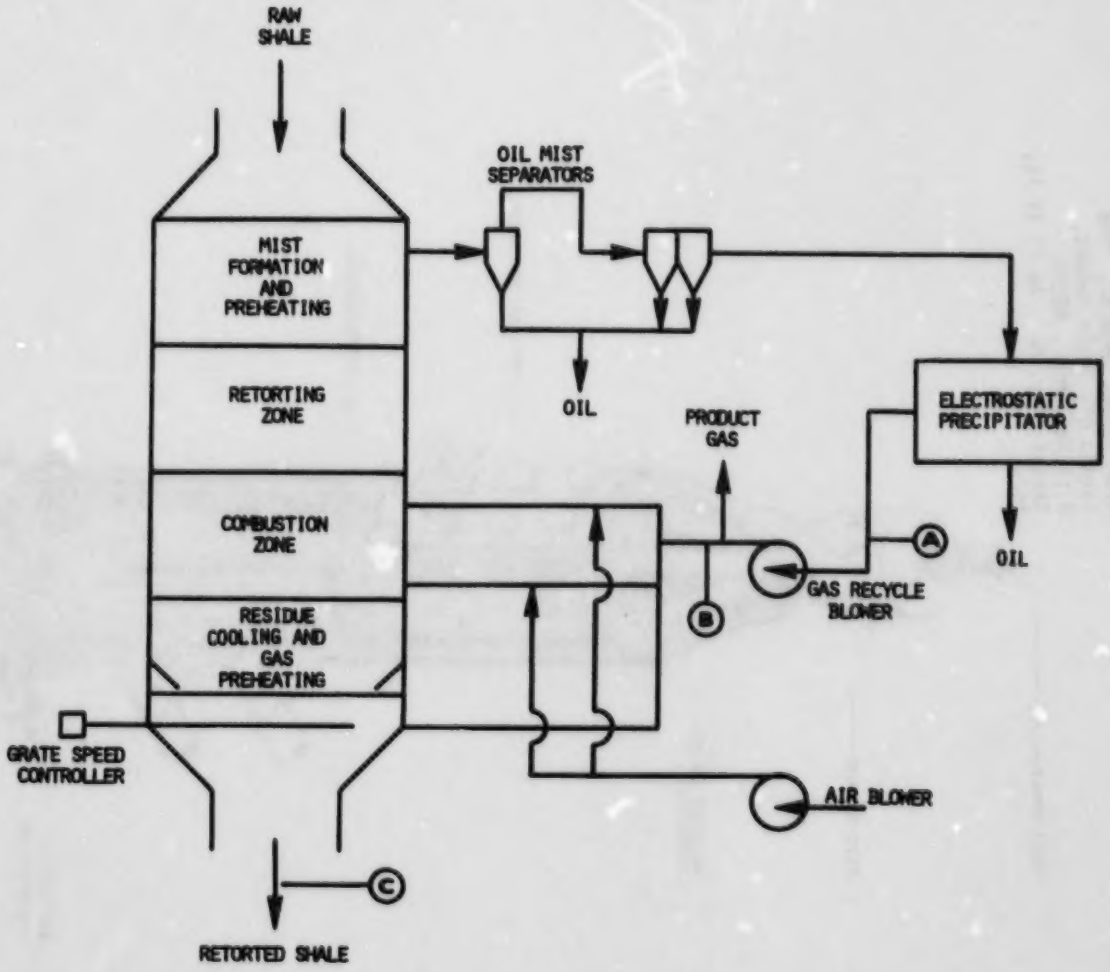

Figure 3. Paraho direct mode flow diagram (pilot plant operation)

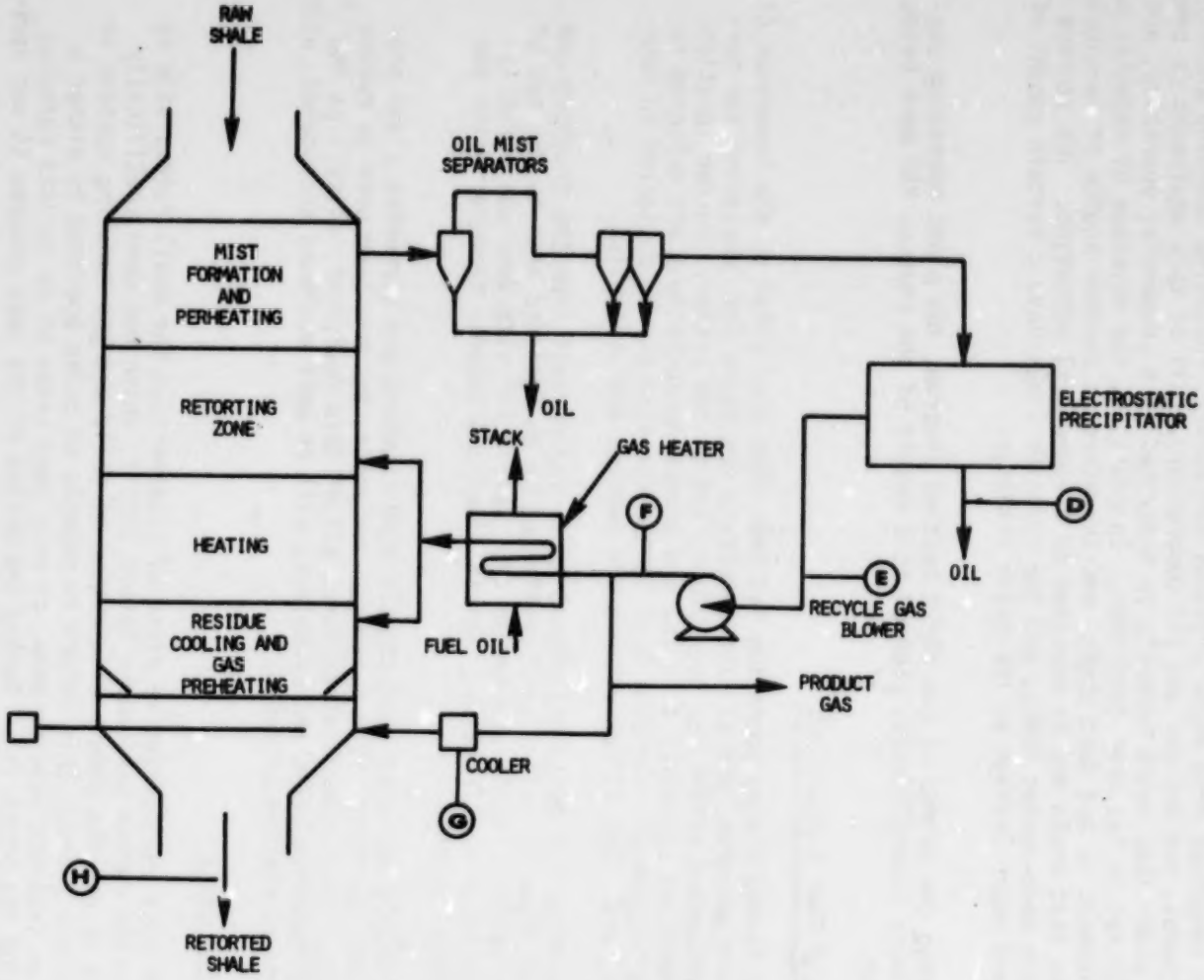

Figure 4. Paraho indirect mode flow diagram (semiworks operation)

has been inherited from these previous operations, including crushing and screening equipment, and the gas and air compressors. All of this equipment is considerably older than would normally be tolerated in a commercial operation, and is certainly not in "as new" condition. In addition, the coverage of material handling movement is not dust tight, and therefore is another source of particulate emissions that would not be expected in a commercial operation. The storage tanks are simple open-vented tanks, and the transfer lines have a certain amount of liquid and vapor leakage at the valve fittings.

During the period of the field testing program, the plant operating conditions were intermittantly changed as a result of the process R&D work being conducted.

Mining and Feed Preparation

The Paraho mining operation had been shut down prior to the inception of the testing program, and all the necessary raw shale for completing the current development effort had been stockpiled at the primary crusher location. The primary and secondary crushing and screening operations are enlcosed in existing buildings. Fugitive dust in the interior air is collected in baghouse filters. The filtered fines are removed and stockpiled.

The minus 7.6 mm (3 in) plus 6 mm (¼ in) product from the crushing and screening plant is lifted and transferred by an inclined belt to the top of the two retorts. Shale crushed to this particular size does not visually appear to cause much dusting. The inclined and lateral transfer belts are not tightly enclosed.

It should be noted that the old USBM crushing and screening plant presently used by Paraho is not typical equipment, but has been used to reduce R&D costs. In a commercial venture, all of this equipment, as well as the material handling belts and elevators, will be well enclosed and sealed, with dust removal systems attached.

Semi-Works Plant

The most representative piece of equipment at the Anvil Points site is probably the Paraho semi-works retort itself, which has been specifically designed to use the same configuration of solid and gas handling systems as a full-scale plant. This retort is capable of being operated in either a direct or indirect heating mode, at mass feed rates of up to 3423 kg/hr-sq meter (700 lbs/hr/sq ft). During the period of the test program it was operated in the indirect mode only.

In indirect-mode operation the retort off-gas, after removal of oil, is compressed and reheated in a process heater before being introduced into the vertical kiln. The present process heater is fired with conventional fuel oil. The semi-works plant make-gas is sent to a thermal oxidizer for combustion. The resulting flue gas is discharged to the atmosphere. No attempt is made to recover by-product sulfur or ammonia.

Spent retorted shale is removed from the bottom of the kiln and transferred by a belt conveyor to the retorted shale disposal area.

Pilot Plant

The pilot plant retort at the Paraho site has been used primarily as a source of essentially inert gas for blanketing the semi-works retort during startup and shutdown conditions. Since the pilot plant is operated in the direct mode, it offered the opportunity during the test program of conducting sampling and emissions testing in that particular mode.

Like the semi-works retort the pilot plant has a nominal throughput capacity of 3423 kg/hr/sq meter. In the direct mode a portion of the residual carbon on the retorted shale is burned to generate the heat for retorting. The off-gas, after separation of oil, is also sent to the thermal oxidizer.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The sampling and analysis research program described in this report constitutes a preliminary effort that has laid the groundwork for more extensive programs that are still in the planning stage. In spite of the preliminary nature of the work, it was successful in accomplishing the first multi-media sampling and analysis undertaking in a shale oil recovery facility.

The test program was in keeping with current multi-media level field testing philosophy within the Industrial Environmental Research Laboratory (IERL) of EPA, according to a recent procedures manual.*

A Level 1 test, as described in the manual, is designed as an initial effort to obtain preliminary environmental assessment information, identify problem areas and set priorities for additional testing. A subsequent Level 2 procedure would be oriented towards identification and quantification of specific compounds, using the knowledge gained from Level 1. Finally, in the longer term, a Level 3 program would involve continuous monitoring of indicator compounds.

The sampling and analysis program conducted at the Paraho site was primarily a Level 1 type of effort, with the test findings intended for input to a Level 2 test plan whenever further process research is conducted at the demonstration plant. The principal conclusions of the reported work relate to comparative effectiveness of sampling and analysis methods; costs and manpower involved in specific procedures; and especially an order-of-magnitude determination of constituents that can be used for later selection of testing accuracy and sensitivity requirements.

One of the major objectives of the testing program was the development of a prototype sampling procedure. Consequently a number of different sampling procedures were used and repetitive samples taken. Not all of the sampling techniques proved applicable and some modification in methodology is recommended in future test work. Collection and analysis of the recycle gases for trace organics proved to be the most complex problem.

*IERL-RTP Procedures Manual: Level 1 Environment Assessment, EPA-600/2-76-160a, June 1976.

The qualitative analytical results obtained are probably more significant than the quantitative data. Various retorting emission constituents have been postulated by others, without any experimental evidence. This test program has helped identify the relative split of trace elements in the retorting products. Arsenic, for example, is usually found in raw shales. From the test results, it appears that trace amounts of arsenic will be found in retorted shale and dusts, and the process water; no arsenic was detected in the recycle gas. Other gaseous-phase measurements were unable to detect COS or CS_2. Each of these respective measurements was accomplished by solution absorption and wet chemical analysis.

Now that a considerable amount of information has been gathered on the qualitative nature of various process streams in the Paraho demonstration plants, future work should focus on quantitative determination of those constituents that may appear in a process residual. Longer-term monitoring programs will be needed, in order to characterize the process throughout its range of operation, rather than at one point in time. The scope of subsequent testing programs should be expanded to include particulate and gaseous measurements during mining and blasting; upwind-downwind particulate sampling beyond the plant boundaries; and raw shale sampling coordinated with plant holdup rates and retorted shale sampling.

On-site gas chromatography is recommended to measure inorganic and light-end hydrocarbons in recycle gas streams. Solid adsorbents may be used to capture trace organics after aerosol removal. But studies are needed to determine the selectivity and efficiency of these materials under field conditions.

Finally, it is recommended that biological screening tests of aqueous and solid samples should be conducted, in conformance with EPA published procedures.

SECTION 3

SAMPLING AND ANALYSIS PROCEDURES

TEST PLAN AND EXECUTION

Selection of Sampling Points

The test plan was discussed with Paraho management and ERDA representatives. The meetings between TRW/DRI personnel and Paraho/ERDA personnel were helpful in determining representative sampling of the process operations at Anvil Points, with minimum interference from background sources and previous retorting operations.

Pilot Plant and Semi-works Recycle Gases

Absorption train samples of the recycle gases (Figure 5) were taken at a point between the electrostatic precipitator and the recycle gas blower (Sample points A and E, Figures 3 and 4). This location was chosen because of the moderate pressure and temperature of the recycle gas at this point. These moderate conditions allowed the sample to be drawn through a heated tygon tube, and minimized the leakage problems caused by high pressure and temperature. At this sampling point, the gas is relatively free of oil mist and (in the case of the pilot plant) dilution air.

Positive pressure was an aid to gas sample collection on adsorption tubes. Consequently, a valved tap on the discharge side of the recycle gas blower was selected as a sample point: for the pilot plant, see Point B on Figure 3; and for the semi-works retort, refer to Point F on Figure 4.

Pilot Plant and Semi-works Recycle Gas Condensate

The condensate from the pilot plant recycle gas was collected through a sample condenser (cooled to 0°C) at the discharge side of the recycle gas blower. This point (B on Figure 3) was chosen because it had a positive pressure which allowed the sample to be drawn without a pump, and because the gas is relatively free of oil mist at this point.

The semi-works condensate was sampled from the bottom gas cooler at a temperature of about 67°C. The point at which the condensate is withdrawn from the system is shown on the semi-works retort schematic, Figure 4, as "G."

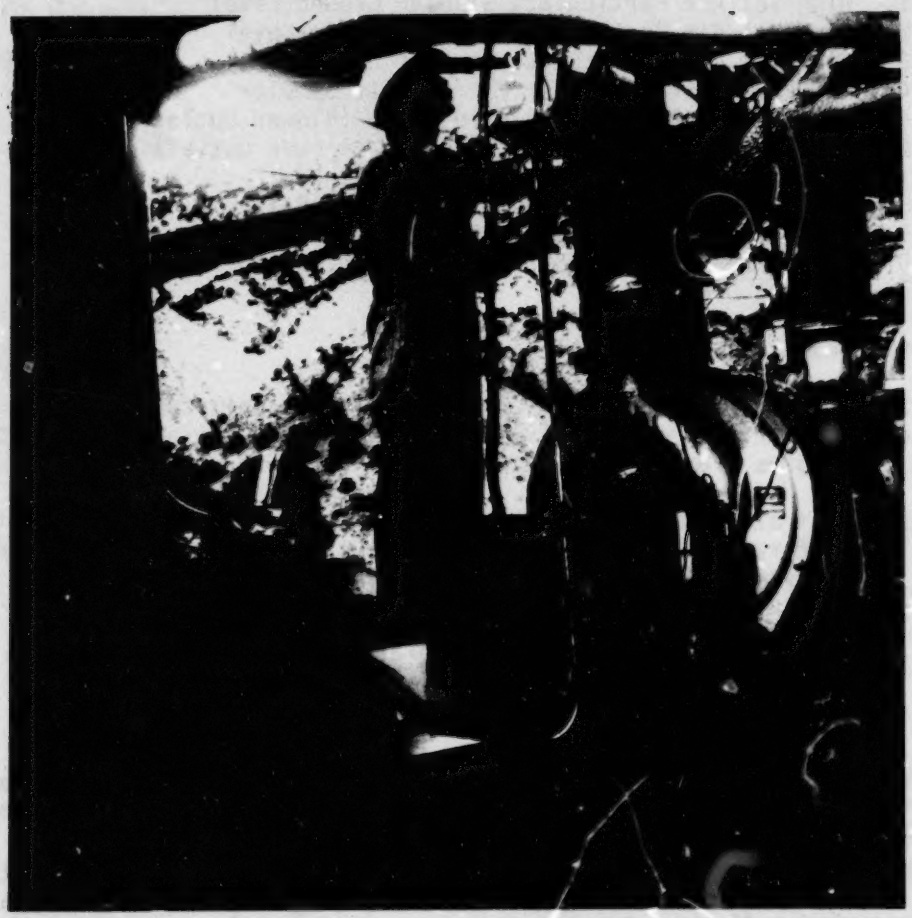

Figure 5. Sampling recycle gases at the semi-works unit.

Crushing Area Particulates

Particulate matter was collected with high volume and low volume samplers positioned near the jaw crusher, primary screen, and the polishing screen. These locations were chosen to give a representative sample of the particulate emissions from this operation. The locations are shown on the plot plan Figure 6, together with other sampling points as follows:

1. High-Vol Air Particulate Sampler Ground Level
2. High-Vol Air Particulate Sampler Upper Level
3. High-Vol Air Particulate Sampler Lower Level
4. Low-Vol Membrane Filter Particulate Sampler
5. Pilot Plant Recycle Gas Stream Tap (Blower Outlet)
6. Semi-Works Recycle Gas Stream Tap (Blower Outlet)
7. Semi-Works Recycle Gas Condensate Tank
8. Pilot Plant Retorted Shale Collection Point
9. Semi-Works Retorted Shale Collection Point
10. Semi-Works Retorted Shale Collection Point
11. Product Oil

Retorted Shale

Semi-works and pilot plant grab samples were collected as close to their respective retorts as physically possible, from the conveyor belt (Points C and H on Figures 3 and 4, respectively).

Lists of all samples taken and removed from the Anvil Points site were reported to Paraho management. These reports included type of sample, date and time the samples were taken, and anticipated analysis technique. These are included in Appendix Section C.

Sampling Procedures and Methods

Recycle Gas Stream, Adsorption Samples

Organic vapor samples were drawn through tubes (MSA* tubes, Tenax,** Bendix charcoal flasher tubes) using a Bendix permissible air sampling pump and calibrated rotometer assembly. Quadruplicate samples were taken for each adsorbent type for 1 and 5 minute sampling durations. Samples were taken directly at the recycle gas sampling ports, and after the gases had been passed through an ice-cooled teflon condenser. Tubes were capped for storage.

Recycle Gas (cold) Condensates

The ice-cooled teflon condenser discharge was put into ice-jacketed quart glass bottles for collection of water and light ends. The bottles had been previously HNO_3-washed and distilled water rinsed.

*Mine Safety Appliances, Inc.
**Applied Science Corp, Mfg.

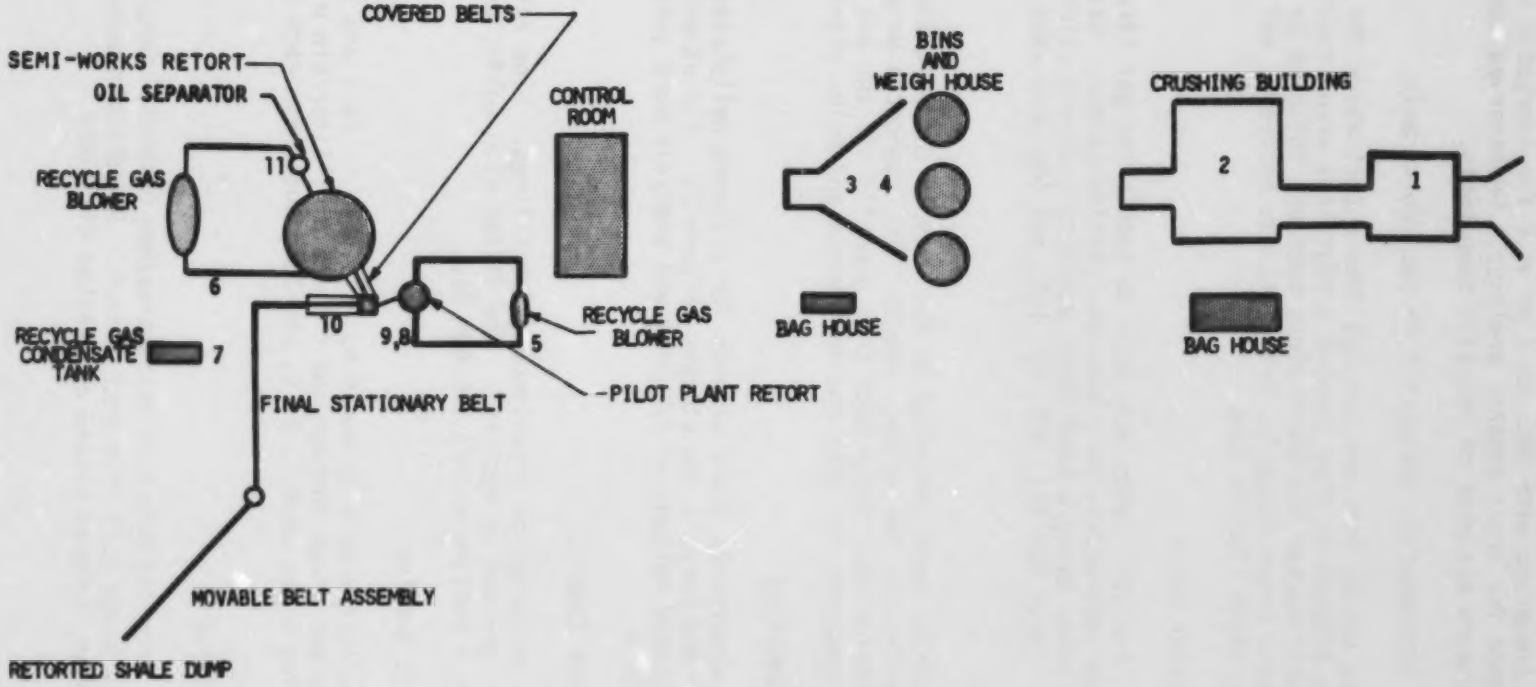

Figure 6. Sample point locations on plan view.

Samples were preserved with HNO_3 to a pH of 2 for inorganic trace analysis or with benzene for trace organic analyses. Unpreserved samples were collected for headspace analyses of volatile components.

Recycle Gas (hot) Condensates, Indirect Mode Semi-works Only

The bottom gas cooler tank was sampled from a port above the tank bottom. The condensate was allowed to flow through a stainless steel cooling coil and was collected in acid-washed one quart glass bottles, followed by sample preservation. Inorganic trace analysis, trace organic analysis, and volatile component analysis could then be done.

Bendix Gastec Analyzer Tubes

Bendix Gastec Analyzer tubes were used to sample the gas streams of both the pilot plant and semi-works, as a semi-qualitative backup. Gases were drawn through the tubes using a hand pump, yielding a direct colormetric reading. Specific tubes for NH_3, HCN, CO, H_2S, and SO_2 were used.

Gas Bottle Samples

250 ml gas bottles were connected to the recycle gas port and allowed to purge for approximately ten volume changes. The stopcocks were then sealed. Triplicate samples were taken both from directly off the gas stream and after the teflon condenser for both the semi-works and pilot plant.

Absorption Train Sampling

Standard EPA absorption train methods for criteria pollutants (SO_2, SO_3, NO_x) were used for the recycle gas streams (Figure 7). For other constituents, commonly accepted methods of sampling and analysis were used, as summarized in Appendix A.

High Vol Particulate Samples

Samples were collected on preweighed glass filters. Flow rates were taken at the start and end of each run. The filter with collected sample was then sealed in a benzene-washed storage bag.

Low Vol Particulate Samples

These were collected on 0.2μ and 0.8μ Millipore filters and 0.2μ Nucleopore filters. Air was drawn through the filters at 1 liter/min with a sampling pump. Sampling times were 1, 2, 5, and 10 minutes for each sampling location.

Retorted Shale Samples

Grab samples were collected in benzene-washed buckets. Samples were taken from the discharge belt from each retort. Immediately upon filling, the cans were lidded, crimped closed and sealed with tape.

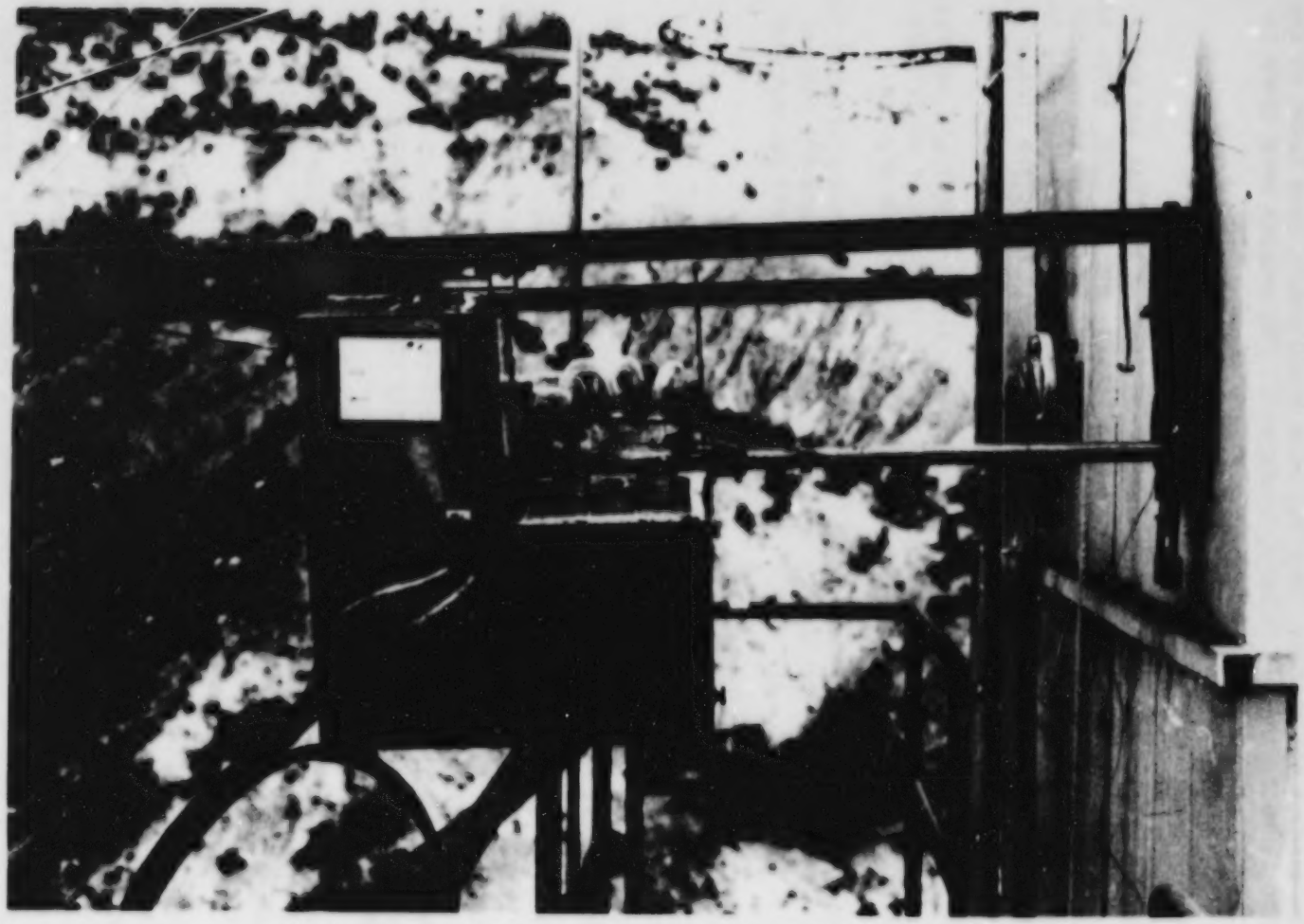

Figure 7. Impinger sampling train mounted in position.

Product Oil

The product oil samples, together with bound water, were taken at the collection sump of the oil recovery equipment. The samples were taken in glass jugs and immediately capped.

Quality Assurance

During sample collection a data sheet was kept on each gas and water sample. A test number was assigned to each sample, and the time, date, sampling location, and volume of sample were recorded. Supporting information and any special sampling procedures were noted on the data sheets. All impingers and sample bottles were thoroughly washed with glassware cleaner, and rinsed with distilled water before each test.

After the samples were collected they were taken to the field laboratory (Figure 8) where they were preserved and transferred to sample containers as necessary. Sample containers were stored in ice chests with dry ice.

Gas absorption and water samples were preserved and then stored in ice chests with dry ice. The samples were shipped to the TRW and DRI laboratories by air freight, and were refrigerated until they could be analyzed.

LABORATORY ANALYSIS METHODS

Analysis Rationale

The general analytical plan for the Paraho samples is illustrated in Appendix Section B. Inorganic, organic, and trace element analyses were done. Most inorganic analyses are standard procedures, using either wet chemistry or atomic absorption techniques. Spark source mass spectrometry (SSMS) was chosen as the most efficient method for trace element analysis, since over 80 different elements can be detected in a single scan.

Organic analyses present a more difficult choice of methods. In addition, qualitative measurements may be the only information obtainable for some constituents.

Based on work carried out at the Denver Research Institute, the use of three interconnected approaches proved to be feasible for the preseparation and analysis of the organic mixtures extracted either from retorted shale or from process water, and the volatile components.

(1) The combination of Gas Chromatography and Mass Spectrometry (GC/MS). This approach is feasible if (a) the boiling points of the components are not too high; (b) the individual components in the GC contain sufficient material to yield a useful mass spectrum; and (c) structural isomers have distinct fragmentation patterns. These requirements restrict, of course, the use of GC-MS in particular in evaluating higher molecular weight compounds and compounds present in the subnanogram range.

Figure 8. Mobile chemical laboratory on site.

(2) The combination of Thin Layer Chromatography (TLC) and/or High Pressure Liquid Chromatography (HPLC) with Mass Spectrometry. In this case the eluted bands or spots from the TLC and/or the collected fractions from repeated separation runs can be used in conjunction with the mass spectrometer using the direct probe method. This method will allow the investigation of the higher molecular weight compounds. If the compounds are (or can be made) ultraviolet absorbent and/or fluorescent the method is quite sensitive.

(3) The combination of TLC and/or HPLC with Spectrophotofluoremetry (SPF). While this method is limited to fluorescent compounds it is very sensitive and can be frequently utilized for good quantitative evaluation of very small quantities of material.

A very useful and effective preseparation method which can be used in combination with the above mentioned analytical methods is gel permeation chromatography (GPC). This method (when applicable) is to be preferred over that of the TLC or LC preseparation procedure because of a much higher efficiency in recovery.

Gaseous Samples

Inorganic constituents in gaseous samples from the recycle gas streams were captured in impinger solutions, and analyzed by standard methods. Analyses were done for SO_2, SO_3, NO_x, AsH_3, HCN, NH_3, CS_2, COS and H_2S as described in Appendix A.

Organic components were collected on site in gas bottles and adsorption tubes and later desorbed in the laboratory for subsequent gas chromatography separation and mass spectrum analysis. Volatiles were stripped from condensate samples and analyzed in the same fashion. Representative traces from GC and MS analyses are included in Appendix B. Most of the information obtained was qualitative.

Water Samples

These samples included recycle gas condensate (hot) taken from the bottom gas cooler, condensate (cold) obtained from a gaseous sample stream condenser, and process water separated from the product oil. Hot condensate was analyzed directly for non-specifics (total organic carbon, BOD, etc.) and major inorganic constituents by standard wet chemistry and atomic absorption methods, referenced in the Appendix B. Trace element analysis was performed on condensates and process water by spark source mass spectrometry, following solvent extraction to remove interfering constituents.

The liquid phases (condensate water and process water) contain organic constituents consisting of water soluble acids, neutrals and bases. The determination of these fractions can be accomplished in a number of ways. An extraction method was used, backed up by total organic carbon analysis (TOC), a straightforward gravimetric method.

Note that the analysis of the recycle condensates and process water requires that the oil-water separation be carried out under identical physical conditions and for the same length of time after sampling, to obtain reproducible results. This is because the amount of organic material distributed between the oil phase and aqueous phase will vary with time and physical conditions.

Following the organic separations, high pressure liquid chromatography (HPLC) and thin layer chromatography (TLC) analyses were conducted. The TLC analytical scheme was used primarily to separate polynuclear aromatic hydrocarbons (PAH), followed by identification and quantification by spectrophotofluorometric (SPF) analyses. Typical TLC and SPF patterns are included in Appendix B.

Solid Samples

The analysis scheme for retorted shale and high-vol collected extractables, trace elements, and volatiles were done in a manner similar to water sample procedures. Although most organic analyses were qualitative, one PAH compound (benzo(a)pyrene) was determined quantitatively by spectrophotofluorometry. This compound was chosen because of data available from other types of retorted shales.

Water extractions of the retorted shale were done to provide an estimate of the total amount of water soluble inorganics present and thus the potential maximum leachability of the material.

Particle size determinations of low-vol collected particulates were done with a scanning electron microscope. Larger particles were determined on site with cascade impaction collector.

SECTION 4

SUMMARY OF ANALYSIS RESULTS

GASEOUS SAMPLES

The analysis results for recycle gas (pilot plant and semi-works) are summarized in Table 1.

The measured values appear to be within expected ranges, as compared to some earlier measurements made at the Paraho site during direct mode operations of the semi-works retort in 1975. It can be seen that NH_3 concentrations in the recycle gas are higher in the indirect mode. Arsine, carbon disulfide, and carbonyl sulfide were not detected in the recycle gas stream from direct-mode pilot plant operations, within the sensitivity of the measurement techniques. A data dispersion and error analysis of these measurements is included in Appendix A.

The trace organic components in the recycle gas stream posed a number of problems both with respect to sampling methods and analysis. A large number of samples were analyzed, and some typical instrument traces are included in Appendix B. In general, all gaseous samples for organic analysis were subjected to GC-MS tests whenever feasible. The GC column used for these separations had a C_5 cutoff. Typical C_4 and lighter compositions of retort gases have been reported elsewhere.*

Qualitatively, the chromatograms from the various samples collected during the direct and indirect modes of operations were about the same. The ratio of the components differed. Quantitative data for the individual components were not obtained since this would have required a calibration of the flame ionization detector response for a wide variety of various reference compounds. In addition, the Tenax sampling tubes were saturated with sample, consisting primarily of aerosols. Quantification of such samples would inevitably contain error. These observations point to the need for more sophisticated approaches to process stream sampling in future test work, and particularly a need for separation of light and heavy components during sample collection.

Table 2 presents a summary of the compounds identified in the recycle gas streams. These compounds are essentially identical to those collected from the water samples headspace analysis and the supernatant oily layer except for relative intensities (concentration) in the mixture. Various GC compounds were identified by mass spectral analysis.

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*Jones, John B., "The Paraho Oil Shale Retort," 81st National Meeting, A.I.Ch.E., Kansas City, Mo., April 1976.

TABLE 1. RECYCLE GAS ANALYSIS FROM SELECTIVE ABSORPTION

Component / Date/Time	SO_2 ppmv	NH_3 ppmv	NO_x ppmv	AsH_3 ppmv	COS/CS_2 ppmv	H_2S ppmv	CO_2 vol. %	CO vol. %	O_2 vol. %
3/9, 13:30-14:45	14		9						
3/9, 15:00-15:45	4		16						
3/10, 10:00-14:00				ND**		2600 (Bendix tube)			
3/11, 10:00-14:00				ND			24.5	2.1	ND
3/11, 15:00		1614							
3/11, 16:00		2689							
3/12, 16:00					ND				

Pilot Plant (Direct Mode) March 9-12, 1976

Shale feedrate: 0.91 tonne/hr (1 ton/hr)*
Average Fischer assay: 116 liter/tonne (28 gal/ton)
Recycle gas rate: 493 std cu meters/hr (290 SCFM)

Component / Date/Time	SO_2 ppmv	NH_3 ppmv	NO_x ppmv
3/14, 15:00	773		
3/14, 17:00	328		
3/15, 12:00		25,945	
3/15, 16:00		27,642	
3/15, 17:00			30
3/15, 17:15			37
3/15, 17:30			49

Semi-Works (Indirect Mode) March 14-15, 1976

Shale feedrate: 10.2 tonne/hr (11.2 ton/hr)
Average Fischer assay: 116 liter/tonne (28 gal/ton)
Recycle gas rate: 6230 std cu meters/hr (3650 SCFM)

*1 tonne = 1000 Kg
**ND = Not Detected

TABLE 2. TRACE ORGANICS IDENTIFIED BY GC/MS IN THE RECYCLE GAS STREAM (DIRECT AND INDIRECT MODE) SUMMARY OF ALL SAMPLES

Peak Number	Boiling Point (°C at 760 mm)	Compound	Molecular Weight
1	36	Pentane	72
2	69	Hexane	86
3	80.1	Benzene	78
4	93-98	Heptenes	98
5	98.5	Heptane	100
6	110.6	Toluene	92
7	121-129	Octenes	112
8	125.6	Octane	114
9	136.2	Ethyl benzene	106
10	138.3	p-Xylene	106
11	139.1	m-Xylene	106
12	140.6	Cyclooctatetraene	104
13	144.5	o-Xylene	106
14	145-146	Styrene	104
15	150.8	Nonane	128
16	161-165	Methyl ethyl benzene	120
17	163.4	a-Methyl styrene	118
18	164.7	1,3,5-Trimethyl benzene	120
19	169.4	1,2,4-Trimethyl benzene	120
20	170.6	1-Decene	140
21	174.1	Decane	142
22	178	Indan	118
23	181	1,3-Diethyl benzene	134
24	182.6	Indene	116
25	192.7	Undecene	154
26	195.6	Undecane	156
27	213.4	Dodecene	168
28	216.3	Dodecane	170
29	218	Naphthalene	128

LIQUID SAMPLES

Three types of liquid samples were collected: (a) cold condensate (from sample condenser), (b) hot condensate (from bottom gas cooler of semi-works retort), and (c) process water separated from the crude shale oil. The condensates contained an oily component which separated out upon standing.

Inorganic analysis results for both semi-works and pilot plant condensates are presented in Table 3. Trace element analyses for cold condensates and process water are included in Table 4.

For clarity of presentation, the results of the inorganic analyses for both the pilot plant and semi-works unit are classified into five different groups in Table 3: cations, anions, nutrients, gross parameters and trace elements. Under each group or category of cations and anions, only the more significant constituents are identified and quantified. Ammonia nitrogen, total Kjeldahl nitrogen (TKN) and phosphorus are classified under the nutrient category because of their eutrophication potential in receiving waters. Gross parameters include constituents that are not readily identified singly but are quantified under group categories. Gross parameters are useful as quality control parameters because of their relative ease of determination. Trace elements included in Table 4 cover those elements that may be subject to water quality regulation.

In general, results of the water analyses from both the pilot plant recycle gas condensate (direct mode) and the semi-works recycle gas condensate (indirect mode) are comparable to those reported in the literature for other retorting operations. As seen in Table 3, the predominant inorganic constituents present appear to be ammonium carbonate and bicarbonates. The presence of a high concentration of ammonia interferes with the standard titrimetric determination for carbonate and bicarbonate alkalinity. Consequently, the carbonate and bicarbonate ions reported in this table are computed values based on the total inorganic carbon (TIC was determined by infrared analysis) and the second ionization constant of carbonic acid at 0.1M ionic strength (Appendix B). The amount of ammonium ion present in the condensates was also computed, based on the ammonia concentration determined by distillation and on the equilibrium constant of ammonia in water. To ensure consistency of data presentation, the equilibrium constant for ammonia was adjusted to 0.1M ionic strength (Appendix B).

An overview of the data from Table 3 shows that there is definite mass imbalance of cations for the pilot plant and of anions for the semi-works plant. To maintain electron neutrality, approximately 840 milliequivalents of cations must be accounted for in the pilot plant and approximately 560 milliequivalents of anions for the semi-works plant. Based on related condensate analyses, it is postulated that organic amines ($R\text{-}NH_3^+$) may be the undetermined anions. Similarly, the presence or organic acids in the semi-works condensate could be a possibility based on the conversion of TOC to equivalent organic acids.

TABLE 3. INORGANIC ANALYSIS OF CONDENSATES (MEASURED AND CALCULATED VALUES)

	Pilot Plant Recycle Gas Cold Condensate (Direct Mode) 3/11/76 - 0800 - 1800 Hrs		Semi-Works Recycle Gas Hot Condensate (Indirect Mode) 3/14/76 - 0800 - 1800 Hrs	
	(mg/l)	(meq/l)	(mg/l)	(meq/l)
CATIONS				
Calcium	60.74	3.03	39.16	1.95
Magnesium	<0.1		<0.1	-
Sodium	0.20	0.009	0.29	0.013
Potassium	0.08	0.002	0.18	0.005
Ammonium (Nh_4^+)	5652-calc.	312-calc.	13540-calc.	752-calc.
ANIONS				
Carbonates	30500-calc.	610-calc.	3030-calc.	61-calc.
Bicarbonates	31265-calc.	512-calc.	6280-calc.	103-calc.
Sulfate	113.6	2.37	1.65	0.034
Sulfide	<0.1		390	24.38
Chloride	TR		TR	
Fluoride	0.35	0.018	0.10	0.005
Nitrate	118	3.03	1.0	0.016
Nitrite	0.02	<0.001	<0.002	
NUTRIENTS				
NH_3-N	14060-calc.	827-calc.	16800-calc.	989-calc.
TKN	31,400	2243		
Phosphate (Total)	0.58		0.75	
GROSS PARAMETERS				
BOD	12,000		4,850	
COD	19,400		17,100	
TOC	29,200		9,800*	
TIC	9,800		1,600	
Oil & Grease	502		33.3	
Solids, Total	22,000		429	
Solids (upon evaporation)	21,800		406	
Solids, Suspended	200			
Total, Alkalinity	68,550		12,900	
Hardness	152-calc.		98-calc.	
Phenols	46		42	
pH	9.8		9.5	

*Semi-works process water total organic carbon (TOC) was 36900 mg/l on 3/15 @ 1500 hrs.
(Note: Blank entries indicate that no calculation or measurement was done)

Operating Parameters for Water Data

	Plant Feed Rate, Tonne/hr (TPH)	Recycle Gas Rate, Std.Cu.Meters/hr (SCFM)
Semi-Works Hot Condensate (3/14/76), 0800-1800 hrs and Process Water (3/15/76, 1500 hrs)**	10.2 (11.2)	6320 (3650)
Pilot Plant Cold Condensate (3/18/76, 1130-1330 hrs) (3/10/76, 0800-1700 hrs)**	0.91 (1.0)	493 (290)

**These operating parameters also apply to Table 4, following.

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are gross parameters that are commonly used to assess the pollution potential of wastewater when discharged. Unacclimated seeds from a sewage treatment plant were used, so that BOD tests were conducted with great difficulty and little precision. Correlation with COD results was also poor. This is particularly true for the semi-works data in which the COD was 17,100 mg/l and BOD was only 4850 mg/l. Future BOD measurements should be done with seeds from a similar water source such as a refinery waste treatment plant.

The conventional method for determining dissolved solids may not be acceptable for these condensates because of the large amount of ammonium carbonates and bicarbonates present. These constituents break down and volatilize readily as NH_3, CO_2, and H_2O at the boiling point of water. Volatile acids may also be lost upon evaporation of water. Based on the above rationale the term "dissolved solids" was discarded and replaced by the term "solids upon evaporation."

The term "total alkalinity" in Table 3 has a different meaning than the traditional one which defines it as the amount of sulfuric acid needed to neutralize hydroxide ions, carbonate and bicarbonate ions. Because of the large amounts of ammonium compounds such as $R\text{-}NH_2$ present, a major portion of the acid is utilized in neutralizing these ammonium compounds. Also, the possible presence of $R\text{-}CO_2^-$ acids reduces the acid requirements that are normally needed for carbonate and bicarbonate neutralization. This may be an explanation as to why there is a significant difference in alkalinity between the pilot plant and the semi-works plant.

Total hardness determination by the conventional (EDTA)* titration method is not possible because of interference from organic substances such as organic acids and amines. Since the major cations contributing to hardness are calcium and magnesium ions, total hardness must be determined instead by computation similar to that described in Standard Methods for water analysis.**

Trace elements analyses were done by spark source mass spectrometry following extraction of organics by benzene (Table 4).

The analysis of condensates and process water for organic constituents included the following:

1. Headspace volatiles over the oily layer
2. The oily layer
3. Volatiles from the aqueous layer of the condensates
4. Total organic carbon (TOC) of the aqueous layers
5. HPLC of the aqueous layer of the condensate

Process water separated out from the product oil within 48 hours, between a denser and lighter organic layer.

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* Ethylenediamine-Tetraceticacid

** Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, D.C.: 13th Edition, 1971.

TABLE 4. CONDENSATE WATER AND PROCESS WATER (SSMS ANALYSIS)

	Cold Condensate Water	Process Water
Element	Pilot Plant µg/ml 3/10/76 0800-1700 Hrs	Semi-Works µg/ml 3/15/76 1500 Hrs
Uranium	0.03	
Lead	0.7	0.2
Mercury	<0.01	<0.01
Praseodymium	0.008	
Cesium	0.01	0.01
Lanthanum	0.04	
Barium	0.1	2.0
Iodine	0.008	
Tin	0.05	
Molybdenum	0.3	0.1*
Zirconium	0.05	
Yttrium	0.007	
Strontium	0.1	3.0
Rubidium	0.4	
Bromine	0.02	0.009
Selenium	0.04	0.1
Arsenic	0.09	1.0
Gallium	0.04	<0.02
Zinc	0.2	0.4
Copper	0.1	0.2
Nickel	0.1	0.2
Cobalt	<0.01	<0.04
Germanium		<0.05
Iron	>10	5.0
Manganese	0.2	0.3
Chromium	0.07	0.3
Vanadium	<0.01	0.03
Titanium	0.9	0.3
Scandium	0.01	<0.05
Calcium	8	>10
Potassium	3	>10
Chlorine	0.4	2.0
Sulfur	3	>10
Phosphorus	0.2	5.0
Silicon	4	>10
Aluminum	0.2	0.8
Magnesium	3	>10
Sodium	5*	>10
Fluorine	-0.1	7
Boron	0.06	-5.0
Lithium	0.02	1.0

*Heterogeneous

After extraction of organics, sample was thermally ashed @ 450°C for ½ hr in a laboratory furnace in a quartz crucible prior to analysis.

Note: See Table 3 for operating parameters.

Organic components identified qualitatively in the condensates and the oily layer were essentially the same as found in the recycle gases (see Table 2). Appendix B includes an example of a HPLC chromatogram for the pilot plant recycle gas condensate after removal of the oily layer. Other HPLC chromatograms are on file at Denver Research Institute. In all of these samples for HPLC analysis, the organic components were removed by passing the condensate and process water through a column of Bondapak 18 and subsequently eluting the organics into a reverse phase HPLC column for separation.

SOLID SAMPLES

Size Distribution

The raw shale particulates were collected by high-vol and low-vol devices in the primary crusher building, in the secondary crusher area, and next to the feed bins and weigh house. Size ranges for raw shale and retorted shale process streams and particulates are given in Table 5 below.

TABLE 5. SIZE RANGES OF SOLIDS

Material	Size Range	Remarks
Raw Feed Shale	<7.62 cm, >6 mm (-3" +¼")	
Fines	<6 mm (¼")	Includes crushing fines
Raw Shale Air Particulates	>0.01 <5 mm	For particle size distribution see Table 6 and 7
Retorted Shale	see below	

Screen Sieve Analyses of Direct Mode
Retorted Shale (3/12/76, 10:00 hrs)

Weight Percent	Sieve Designation Standard (New U.S. Nos.)
26.4	>19.0 mm
9.9	19.0
9.0	13.2
11.5	9.5
4.4	4.75
6.6	3.25
3.2	1.70
6.2	1.18
2.7	600 µm
2.4	425
2.4	300
2.1	212
0.6	150
2.4	106
8.7	75
1.6	<45

A Brink's cascade impaction sampler was used to collect particulate dust in the primary crusher building vicinity (location No. 2 on Figure 6). The mass of particulate collected in each separation stage was plotted according to the calibration relations for the sampler, yielding a particle size distribution as shown in Table 6 below.

TABLE 6. MASS FRACTION OF RAW SHALE PARTICULATES

Particulate Size Range	<0.3 μm	<1.0 μm	<3 μm
Cumulative Weight Percent less than stated size	2	26	73

(Sample taken at 1400 hrs, 3/17/76
crushing 28 gal/ton shale)

Mean particle size (effective diameter) analysis of low-vol air particulate samples was determined by scanning and transmission electron microscopy. Values as percent of particle counted are given in Table 7.

TABLE 7. NUMERICAL FRACTION OF RAW SHALE PARTICULATES

Particulate Size Range	Breakdown % <1.0 μm					
	<0.01 μm	0.01-0.05 μm	0.05-1 μm	Cumulative % <1.0 μm	1-5 μm	>5 μm
Cumulative Count Percent less than stated size	50.4	33.3	1.2	84.9	10.1	5.0

(Sample taken at 1410 hrs, 3/15/76
handling 28 gal/ton shale)

Compositions of Solids

Particulates --

The major components of raw shale particulates of various sizes, taken from low-vol collectors, are shown in Tables 8 and 9. The values in Table 8 are averages of individual particulates, as determined by x-ray fluorescence, and should not be interpreted as mass fractions. These raw shale particulate analyses should be viewed as qualitative since river rock was being crushed prior to the period of shale crushing operation (3/14-3/17). The values in Table 8 indicate that the inorganic constituents tend to be emphasized in finer particulate sizes.

Elemental Analyses --

Table 9 shows an elemental analysis of the direct mode retorted shale, the benzene extract from retorted shale, and that of the particulates from the crushing area. As a comparison, composite analysis of the organic matter from Green River cores is also given, as determined by Laramie Energy Research Center. Trace element analysis of direct mode retorted shale was done by

TABLE 8. PARTICLE SIZE VS. MEAN ELEMENTAL COMPOSITION OF RAW SHALE AIR PARTICULATES AS DETERMINED BY X-RAY FLUORESCENCE

Elemental Components Detected \ Size Ranges of Particles Analyzed	<5 µm*	<1.0 µm	>1, <5 µm	>5 µm
Si	40%	30%	44%	43%
Ca	20	16	24	22
Al	10	11	10	8
Mg	10	12	6	8
Fe	+	9	5	6
K	+	2	5	6
Na	+	2	3	2
P	-	3	+	+
S	+	12	+	4
Ti	+	-	+	+

*High background fluorescence.

+Indicates presence of element but not quantifiable

-Indicates element not found in sample at sufficient concentration to be detected by x-ray fluorescence.

TABLE 9. ELEMENTAL ANALYSIS OF RETORTED SHALE, PARTICULATES, AND ORGANIC EXTRACTS (PERCENT)

	C Total	C Org.	C Inorg.	H	O	N (Dumas)	S (Free)	S (SO_4)	S (Sx)	Ash (dry)
Benzene Extract of Direct Mode Retorted Shale (3/12/76, 1000 hrs)	81.41	81.41	*	10.70	2.22	2.05	7.79	NA	NA	<0.15
Direct Mode Retorted Shale (3/12/76, 1000 hrs)	2.95	0.80	2.15	0.10	ND	0.13	ND	0.08	0.74	92.88
Raw Shale Collected as Air Particulate (3/15/76 to 3/17/76)	14.25	9.58	4.67	1.51	ND	0.43	ND	0.01	0.04	70.91
Organic Matter† in Raw Shale (average of 10 cores from Colorado & Utah)		80.5		10.3	5.8	2.4	1.0			

* 0.5% of total C

ND = Not Determined
NA = Not Applicable

†Smith, J. W., Ultimate Composition of Organic Matter in Green River Oil Shale, USBM RI5725 (1961)

spark source mass spectrometry. The values for the pilot plant shale from direct mode operation are reported in Table 10. In 1975, retorted shale samples resulting from direct-mode operation of the semi-works plant were analyzed by Denver Research Institute under an agreement with Paraho, as part of an NSF contract. Trace element analysis of these samples, done by flameless atomic absorption, are also reported in Table 10.

Organic and Inorganic Extractions and Analyses --

Retorted shale contains various percentages of organic carbon, and various percentages of extractable residual organic matter. The amounts of total organic carbon and benzene extractable organic matter depend on the type of retorting process and the efficiency of retorting. Table 11 shows the total organics extractable by benzene from the direct mode retorted shale, as well as raw shale particulate, and the water soluble component of the retorted shale.

The organic extract from the direct mode retorted shale was preseparated by TLC (Figure 9) in order to determine the ratio of polynuclear aromatic hydrocarbon compounds (PAH) to polar compounds. An example of the TLC chromatogram is shown in Figure 10.

The polar components from the direct mode retorted shale benzene extractables (Table 12) contain phenolics, alcohols, and acids (aliphatic and aromatic acids). The phenols include phenol per se, cresols, naphtols and higher molecular weight phenols. These and the nitrogen compounds have as yet not been separated and identified.

The PAH compounds preseparated from the benzene extract were further separated by two dimensional layer chromatography. An example of the qualitative separation of the PAH compounds from the direct mode retorted shale is shown in Figure 10 and Table 13.

The TLC in Figure 10 is a mixed layer two-dimensional chromatogram. Most of the compound identification is based on R_B values:

$$R_B = \frac{\text{Distance (x,y) from origin to spot}}{\text{Distance (x,y) from origin to BaP spot}}$$

The benzo(a)pyrene spot was confirmed in the spot No. 1 and it was determined quantitatively by spectrophotofluorometry (Figure 11). The values for BaP for the extracts from the direct mode retorted shale are presented in Table 14 and compared to an earlier BaP determination from a direct mode Paraho retorted shale sample.

TABLE 10 TRACE ELEMENT ANALYSIS OF RETORTED SHALES
(VALUES IN PPM)

Element	Direct Mode (Pilot Plant) 3-15-76, 1100 hrs	Direct Mode (Semi-Works)* 3-15-76
Uranium	5	7
Thorium	7	4
Lead	23	24
Mercury*	0.06	0.06
Terbium	0.7	0.6
Gadolinium	1	0.9
Europium	0.7	0.6
Samarium	2	1
Neodymium	6	9
Praseodymium	2	5
Cerium	59	100
Lanthanum	21	33
Barium	180	310
Cesium	6	10
Iodine	<0.2	<0.2
Antimony	0.7	1
Tin	0.2	2
Molybdenum	14	18
Niobium	7	8
Zirconium	65	41
Yttrium	40	17
Strontium	970	760
Rubidium	110	85
Bromine	0.2	0.2
Selenium	0.5	0.4
Arsenic	35	18
Germanium	0.9	<0.2
Gallium	17	13
Zinc	22	17
Copper	57	53
Nickel	75	20
Cobalt	19	15
Manganese	800	700
Chromium	230	110
Vanadium	180	110
Scandium	26	20
Chlorine	43	42
Fluorine	>1000	920
Boron	48	82
Beryllium	2	1
Lithium	85	370

Note: Fe, Ti, Ca, K, S, P, Si, Al, Mg, Na, O, N, C, H are all present in quantities greater than 1000 ppm.

All elements not reported <0.2 ppm by weight

*Flameless Atomic Absorption

TABLE 11. BENZENE AND WATER EXTRACTABLES OF RETORTED SHALE, AND RAW SHALE PARTICULATES

	Total Benzene Solubles Wt %	Benzene Solubles Sulfur Removed Wt %	Water Solubles Wt %	Benzene Solubles of Water Solubles Wt %
Pilot Plant (Direct Mode) Retorted Shale (3/12/76, 1000 hrs)	0.03	0.03	3.39	0.00
Raw Shale Collected as Air Particulate in the Crushing Area (3/15/76 to 3/17/76)	2.05	ND	ND	ND

ND = Not determined

TABLE 12. COMPARISON OF PAH TO POLAR COMPOUNDS IN SOLID SAMPLES

Sample Designation	Wt. % PAH	Wt % Polar Compounds
Pilot Plant Retorted Shale, Direct Mode (3/12/76, 1000 hrs)	43	57
Raw Shale Air Particulate (3/15/76 to 3/17/76)	16	84

TABLE 13. R_B VALUES FOR PAH FRACTION OF BENZENE SOLUBLES FROM DIRECT MODE RETORTED SHALE

Spot No. on Figure 10	Fluorescence	R_B I	R_B II	Compound
1	purple	1.00	1.00	*Benzo(a)pyrene
1 (tailing)	purple	0.79	1.02	*Benzo(a)pyrene
2	light blue	1.02	1.25	**Coronene
3	blue	0.93	1.27	
4	yellow	0.87	1.45	
5	purple	0.95	1.64	**1,2 Benzanthracene
6	blue	0.83	1.89	
7	purple	1.08	1.95	**1,2 Benzanthracene
8	blue	1.19	1.84	
9	purple	1.36	1.91	**Pyrene
10	blue green	1.24	2.18	**Fluoranthene
11	purple	1.38	2.34	
12	purple	1.27	2.80	
13	blue	0.31	2.41	
14	blue	0.00	2.34	

*Quantitatively identified by fluorescence spectrometry and/or high pressure liquid chromatography.
**These compounds have been qualitatively identified by R_B values only.

TABLE 14. EVALUATION OF BENZO(A)PYRENE CONTENT IN SAMPLES OF BENZENE EXTRACTS FROM DIRECT MODE RETORTED SHALES

Sample Designation	Bz. Sol. Quantity Analyzed (mg)	BaP/TLC Spot (µg)	Wt % BaP in Bz. Solubles	BaP in Bz.Sol. (µg/kg)	BaP in Shale Sample (µg/kg)	BaP in Bz. Sols. ppm	BaP in Sample ppm
Pilot Plant (Direct Mode) Retorted Shale (3/12/76, 1000 hrs)	8.7	0.050	.000	4.7×10^3	2.0	4.7	0.2×10^{-2}
	8.7	0.038	.000	3.6×10^3	1.5	3.6	0.2×10^{-2}
	Ave.	0.044	.001	4.2×10^3	1.8	4.2	0.2×10^{-2}
Retorted Shale (Direct Mode) Semi-Works (3/75)	Ave.	0.189	0.001	14×10^3	1.50	14	0.2×10^{-2}

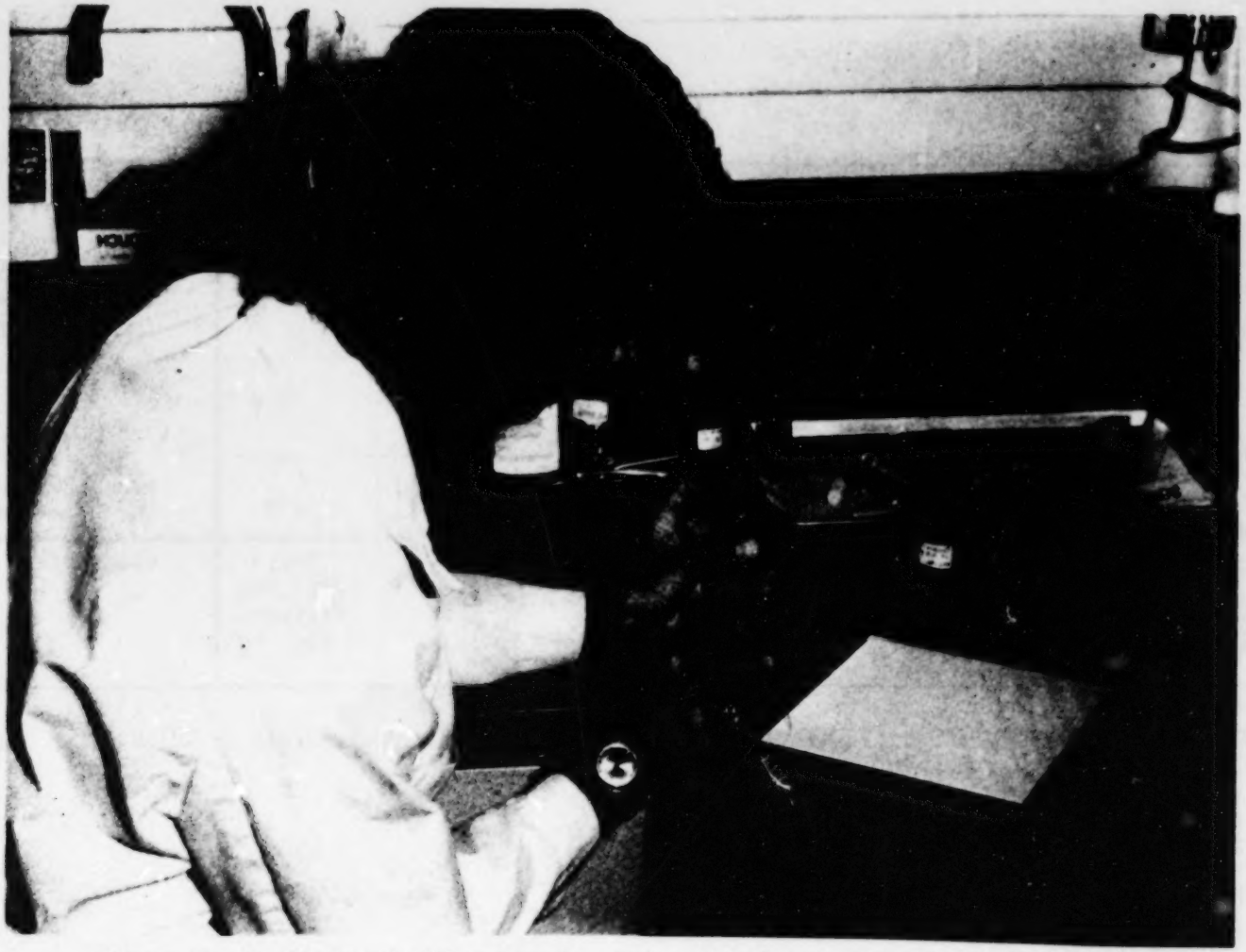
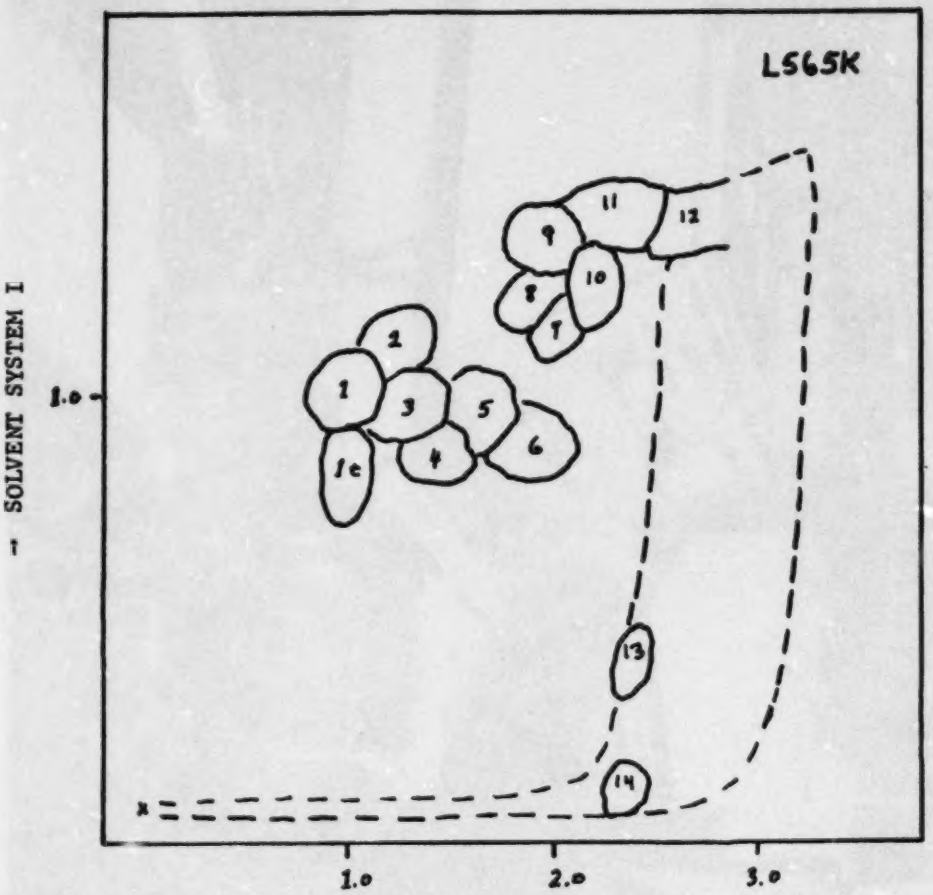


Figure 9. Analysis of PAH compounds, using thin layer chromatography techniques.



Two dimensional mixed thin layer chromatogram of the PAH fraction of benzene solubles from direct mode retorted shale (3/12/76, 1000 hrs). Layer: 40% acetylated cellulose, aluminum oxide G, silica gel G (1:1:1). Solvents: System I, isooctane, drying followed by n-hexane, benzene (95:5). System II, methanol, ether, water (4:4:1). Compounds: 1 and 1 tailing, benzo(a)pyrene.

Figure 10. Mixed layer two-dimensional chromatogram.

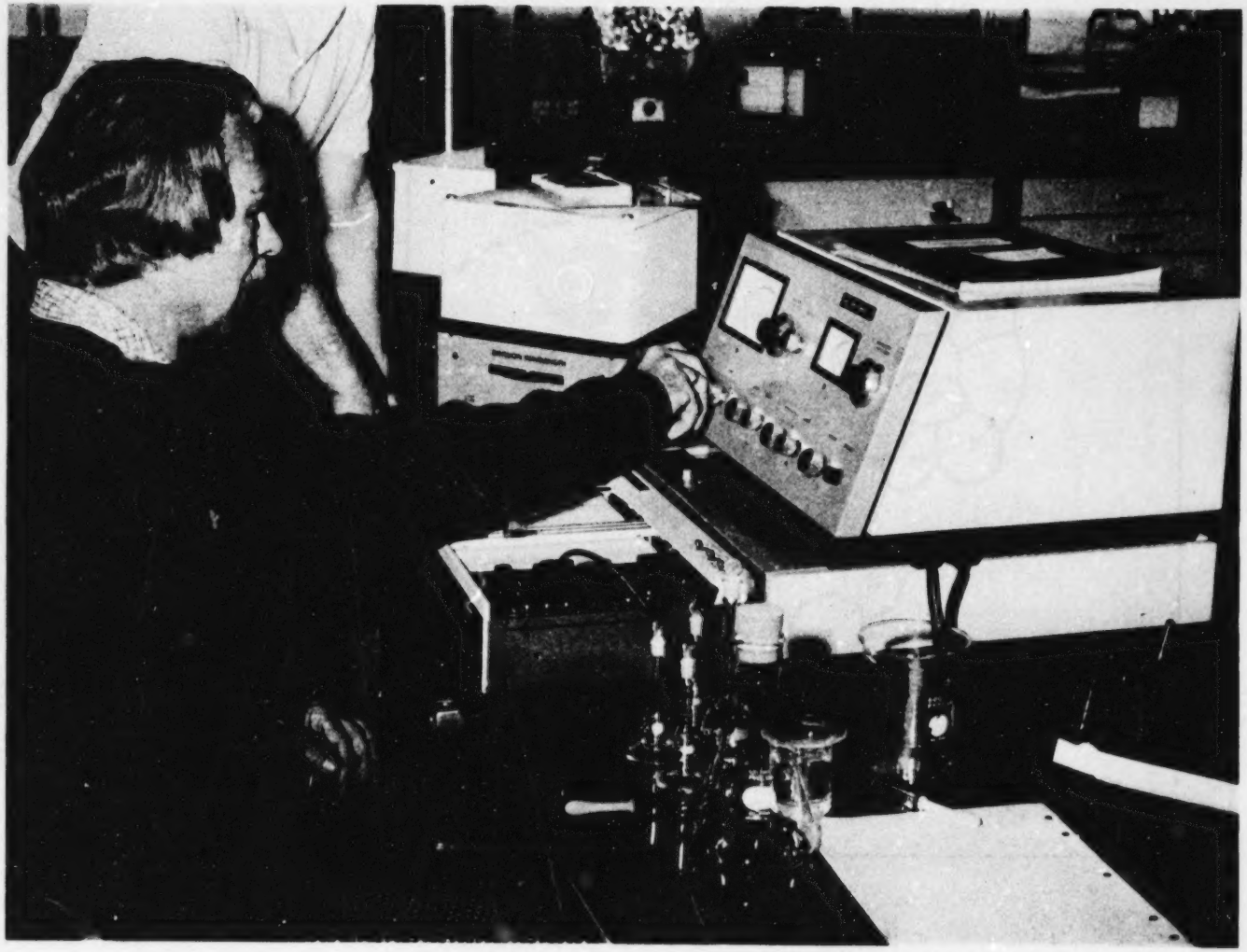


Figure 11. Determination of PAH compounds with spectrophotofluorometry.

SECTION 5

DISCUSSION OF PROCEDURES AND RESULTS

SAMPLING PROCEDURES

Condensates

Condensates were taken out of the bottom gas cooler ("hot") or extracted from the recycle gas stream ("cold") with an ice-cooled sample condenser. Both samplings provide useful information, but it must be clearly understood in all data reporting that these two types of condensate are quite different Lighter components will be condensed out at 0°C, but may be above their dew point at process cooler conditions. Condensates collected in future sampling programs should be quickly frozen and kept in the frozen state until they are analyzed, as a precaution against loss or organic volatiles. No other sample preservation requirements than those described in the report appear to be needed.

Retorted Shale

Retorted shale grab samples were taken directly off the discharge belt, in approximately five kilogram lots. While there are no comparative data for sampling by other methods at Paraho, much larger composite batches should be taken in subsequent sampling efforts. Batch sizes of 100 kg would provide better assurance of representative samples, and the same recommendations apply to raw shale sampling.

Particulates

Particulates from raw shale crushing were collected by high-vol units, although these types of collectors are intended for very low dust concentrations typical of ambient conditions. In much higher dust concentrations, high-vol units were observed to quickly load up to the point where air could not be pulled through. Shorter collection times and more frequent sample removals will be needed. Dust collection was also done with low-vol units and cascade impactors, and in these cases the quantity of sample collected was much smaller than with high-vol units. These same comments are applicable to any future collection of retorted shale particulates where handling or transfer operations occur.

Gas Stream Sampling by Selective Absorption

Conventional sample trains with various absorbing solutions in glass impingers were used as one means of recycle gas constituent collection. These

methods have primarily been used in stack sampling work, where gas constituents are in low concentration. Sample train absorption of recycle gas constituents was satisfactory for the collection of NH_3 and SO_2; but attempts to detect whether or not HCN was present were unsuccessful in the presence of ammonia. Recycle gases contain high concentrations of hydrogen and light hydrocarbons. The sample train exhaust must be vented to a point where the gases do not pose an explosive hazard.

The standard EPA method of NO_x collection by the evacuated flask technique was also satisfactory.

Gas Sample Collection on Solid Adsorbents

Samples were concentrated on charcoal and Tenax (a polymeric material) to provide sufficient sample for GC/MS identification of trace organics in the recycle streams. Since this type of sampling procedure proved to be rather difficult, a more detailed discussion of the procedure is appropriate.

Some considerations to keep in mind for the evaluation of the adsorbent properties of charcoal and Tenax can be summarized as follows:

1. Charcoal

    a. It has a very high collection efficiency for solvent vapors.

    b. It is not suitable for collecting strong oxidants, substances with high vapor pressures, or very polar compounds.

    c. MSA tubes have two charcoal sections and if any significant amount of the sample is found in the reference section, it should be assumed that the adsorption limit of the tube has been exceeded; therefore, the analysis is not quantitative even though the total volume of gas sampled is known.

    d. Less than twenty solvents have been studied for quantitative recovery by solvent (CS_2) desorption.

    e. Up to 95% humidity does not cause any problem, but the presence of water droplets can change the adsorption characteristics of the charcoal.

    f. In a mixture the more polar components may displace the less polar components.

    g. Easy recovery of the organics by CS_2 desorption is the major advantage but the more volatile part of the sample is readily lost.

2. Tenax

   a. If Tenax is to be used for quantitative analysis, its limits with respect to trapping efficiency and recovery need to be established.

   b. Alkanes, alcohols and amines are more efficiently trapped than aldehydes, ketones and phenols.

   c. High molecular weight compounds are more easily retained than low molecular weight substances.

   d. Each substance has a specific affinity for the adsorbent at a given temperature and the quantity adsorbed is characteristic of each substance.

   e. Rate of sampling and temperature were found to have strong effects on displacement but the loss of the more volatile fraction of gaseous samples occurs regardless of the sampling rate.

   f. Samples have been stored for up to 4 months without any apparent change.

The charcoal from the sample tubes could not be removed because the samples were too moist. It was necessary to pass CS_2 through the tube to desorb the sample and thus most likely the more volatile components were lost. Tenax is readily soluble in carbon disulfide, benzene or xylene. Therefore if any of these components (espeically the substituted benzenes) are present, there may be irreversible adsorption. When the recycle gases were sampled, aerosols were probably present in concentrations several orders of magnitude higher than would be found in an ambient air sample.

RECOMMENDATIONS FOR FUTURE SAMPLING AND ANALYSIS

The following recommendations are designed to complement the data in order to complete Level 1 assessment of the Paraho Plant* and prepare for a Level 2 assessment.

1. An on site survey should be made of the facility to review sampling sites and changes that have been made since the previous testing program. This should be done before the plant is in operation to make suggested modifications in sampling ports. These modifications include:

   a. Changing sampling outlets on the recycle gas system to allow for probe insertion.

   b. Installing door-type access to the retorted shale conveyor system at a point as close to the actual retort outlet as possible.

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*Ibid, p10; also, Technical Manual for Process Sampling Strategies For Organic Materials, EPA-600/2-76-122, April 1976.

2. A gas chromatograph/integrator with appropriate detectors should be used to quantitatively measure the inorganic and low molecular weight organic gases of interest in the field. On-site gas chromatography permits evaluation of the sampling methods and reduces the possibility of sample degradation which may occur during transportation to the laboratory. When the chromatograph is fitted with a thermal desorption inlet, evaluation of the trapping efficiency of organics on polymers such as Tenax is possible.

3. Organic compounds extracted from Tenax, solid samples or liquid condensates should be separated by liquid chromatography into the fractions shown in Table 15 for subsequent analysis by infra-red spectrometry and mass spectrometry or combined gas chromatography/mass spectrometry. Gel permeation chromatography and high pressure liquid chromatography are useful separatory methods which provide fractions separated on the basis of molecular weight and functional group.

4. Particulate sample collection should be expanded to include baghouse inlet-outlet air streams, using highly sensitive membrane filter/electron microscopy methods. In addition, each hi-vol sampler location should include paper type sampler, membrane filter assembly and gaseous adsorption tube samplers. Backup particle sizing using gravimetric methods would be useful for verification.

5. Complete Level 1 analysis includes performance of biological screening tests in accordance with the EPA Office of Health and Ecological Effects recommended procedures. Such testing is designed to determine potential health hazards by measuring toxicity, mutagenicity and LD_{50}.

6. The scope of future test work should include particulate and gaseous sample collection in the vicinity of mining operations, and retorted shale handling and disposal areas. Upwind-downwind particulate collection away from the immediate process areas should also be scheduled. Raw shale feed samples should be collected for analysis in conjunction with plant operation schedules and retorted shale sampling.

TABLE 15. CLASSES OF ORGANIC COMPOUNDS ELUTING IN EACH LIQUID CHROMATOGRAPHY FRACTION

Fraction	Compound Type	Solvent
1	Aliphatic hydrocarbons	60/80 petroleum ether
2	Aromatic hydrocarbons PCM PCB Halides	20% methylene chloride in 60/80 petroleum ether
3	Esters Ethers Nitro compounds Expoxides	50% methylene chloride in 60/80 petroleum ether
4	Phenols Esters Ketones Aldehydes Phthalates	methylene chloride
5	Phenols Alcohols Phthalates Amines	5% methyl alcohol in methylene chloride
6	Amides Sulfonates Aliphatic acids Carboxylic acid salts	20% methyl alcohol in methylene chloride
7	Sulfonates Sulfoxides Sulfonic acids	50% methyl alcohol in methylene chloride
8	Sulfonic acids	methyl alcohol

APPENDIX A

ABSORPTION TRAIN SAMPLING AND ANALYSIS METHODS

ARSINE (AsH_3)

The gas sample was drawn through four impingers in series in an ice bath. The first impinger was packed with glass wool impregnated with lead acetate solution to remove H_2S. The second and third impingers contained decinormal NaOH. The fourth impinger contained silica gel.

The pilot plant recycle gas was sampled with the first impinger packed with glass wool impregnated with lead acetate. The second and third impingers contained 25 ml of 0.1 N NaOH. The last impinger contained 20 g of silica gel. The sampling rates for the first and second tests were 0.39 liter per minute and 0.35 liter per minute, respectively.

Reference: Furman, H. Howell, Scott's Standard Methods of Chemical Analysis, 6th Ed., Princeton, 1962, p. 137.

HYDROGEN SULFIDE (H_2S)

Sample gas was drawn through four midget impingers in series, held in an ice bath. The first two impingers contained alkaline $CdCl_2$ solution (20g $CdCl_2$, dissolved in 900 ml of water to which was added 20 ml of 0.5 N sodium hydroxide solution). The third impinger was left dry to catch carryover droplets, and the last impinger contained silica gel.

In sampling the pilot plant recycle gas midget impingers were used. The first two impingers each contained 20 ml of absorbing solution, the third impinger was dry, and the fourth impinger contained 20 g of silica gel.

Samples of the pilot plant recycle gas were taken over a one hour period at a sample flow rate of 0.4 liter per minute.

Reference: Air Pollution Control District, County of Los Angeles, Air Pollution Source Testing Manual, 1963, pp. 87-88.

CARBONYL SULFIDE (COS)

The pilot plant recycle gas was sampled with a set of four impingers in series kept in an ice bath. The first impinger contained glass wool impregnated with lead acetate, the second impinger contained 20 ml of 7.5% $CaCl_2$ with 1% ammonium hydroxide to capture COS, and the third contained 20 ml of alcoholic KOH to collect CS_2. The last impinger contained silica gel.

Sampling was done for a twenty minute period at a sampling rate of 0.22 liter.

Reference: Jacobs, Morris B., The Chemical Analysis of Air Pollutants, New York, 1960, p. 192.

SULFUR DIOXIDE (SO_2) AND NITROGEN DIOXIDE (NO_2)

Reference: U.S. Environmental Protection Agency, Standards of Performance for New Stationary Sources, Federal REgister, Vol. 36, No. 247, Part. 60.85.

AMMONIA (NH_3)

Sample gas was drawn through four impingers in series, held in an ice bath. The first impinger contained distilled water. The second impinger contained 5% HCl solution. The third impinger was left empty to collect carry over droplets. The fourth impinger contained silica gel.

In sampling the semi-works recycle gas midget impingers were used containing 25 ml each of distilled water and 5% HCl in the first and second impingers, respectively. The last impinger contained 20 g of silica gel. The sampling rate was .2 liter per minute, and the test was run for one hour.

The pilot plant recycle gas test was run with midget impingers in the same way that the semi-works recycle gas test was done. The sampling rate was 1.27 liters per minute during the first test and 0.66 liter per minute during the second test.

Reference: Air Pollution Control District, County of Los Angeles, Source Testing Manual, 5th Ed., (1972), sec. 5.4.1.

TABLE A-1. GAS ABSORPTION SAMPLE DATA DISPERSION ANALYSIS

Test No.	Measured Value (ppmv)	Arithmetic Mean	Difference	Standard Deviation	Student's "t"	Level of Significance
NH_3-SW-1	25,945	25066	879	5936	0.3	0.75
NH_3-SW-2	27,642		2576		0.9	0.55
NO_2-SW-4	30	39	-9	9	1.7	0.20
NO_2-SW-5	37		7		0.4	0.75
NO_2-SW-6	49		10		1.9	0.15
NO_2-1	9	11	-2	3.5	1.4	0.2
NO_2-2	9		-2		1.4	0.2
NO_2-3	9		-2		1.4	0.2
NO_2-4	9		-2		1.4	0.2
NO_2-5	14		3		2.1	0.07
NO_2-6	18		7	(x + 20)	4.9	0.003

TABLE A-2. GAS ABSORPTION SAMPLES - SYSTEMATIC ERRORS IN ANALYSIS

Test #	Analytical Accuracy (± mg)	Volume of Gas Samples (ft^3)	(± ppmv)	Test Accuracy (% of measured value)
NH_3-SW1	± 6.6 mg	0.409	790	3
NH_3-SW-2	± 8.6 mg	0.419	1005	3.6
NH_3-1	± 2.3 mg	2.178	52	3.2
NH_3-2	± 4.9 mg	1.121	214	7.8
NO_x-SW-4	.003	0.053	1	3
NO_x-SW-5	.003	0.048	1	3
NO_x-SW-6	.004	0.052	1.5	3
NO_x-1	.001	0.05	0.3	3
NO_x-2	.001	0.05	0.3	3
NO_x-3	.001	0.048	0.3	3
NO_x-4	.001	0.044	0.3	3
NO_x-5	.001	0.046	0.4	3
NO_x-6	.001	0.038	0.5	3

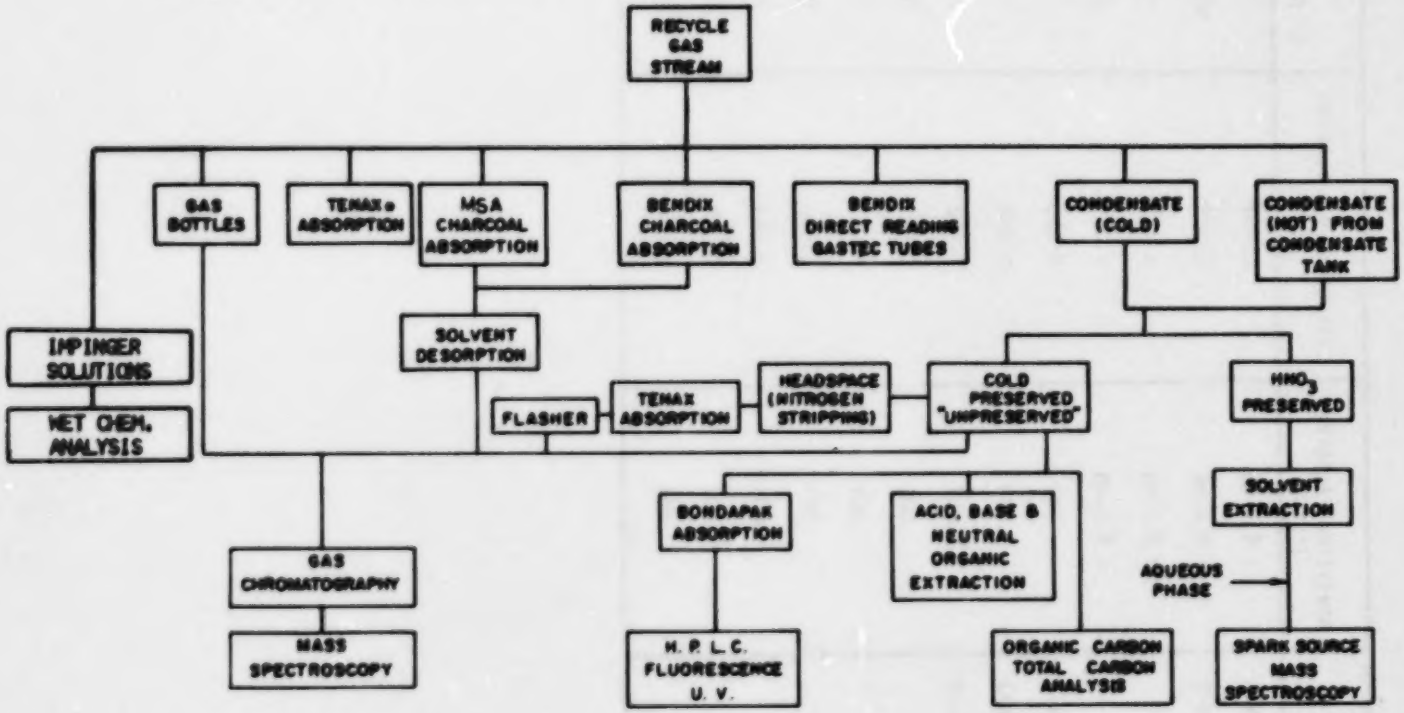
APPENDIX B

LABORATORY ANALYSIS METHODLOGY AND DATA

ANALYTICAL SCHEMES

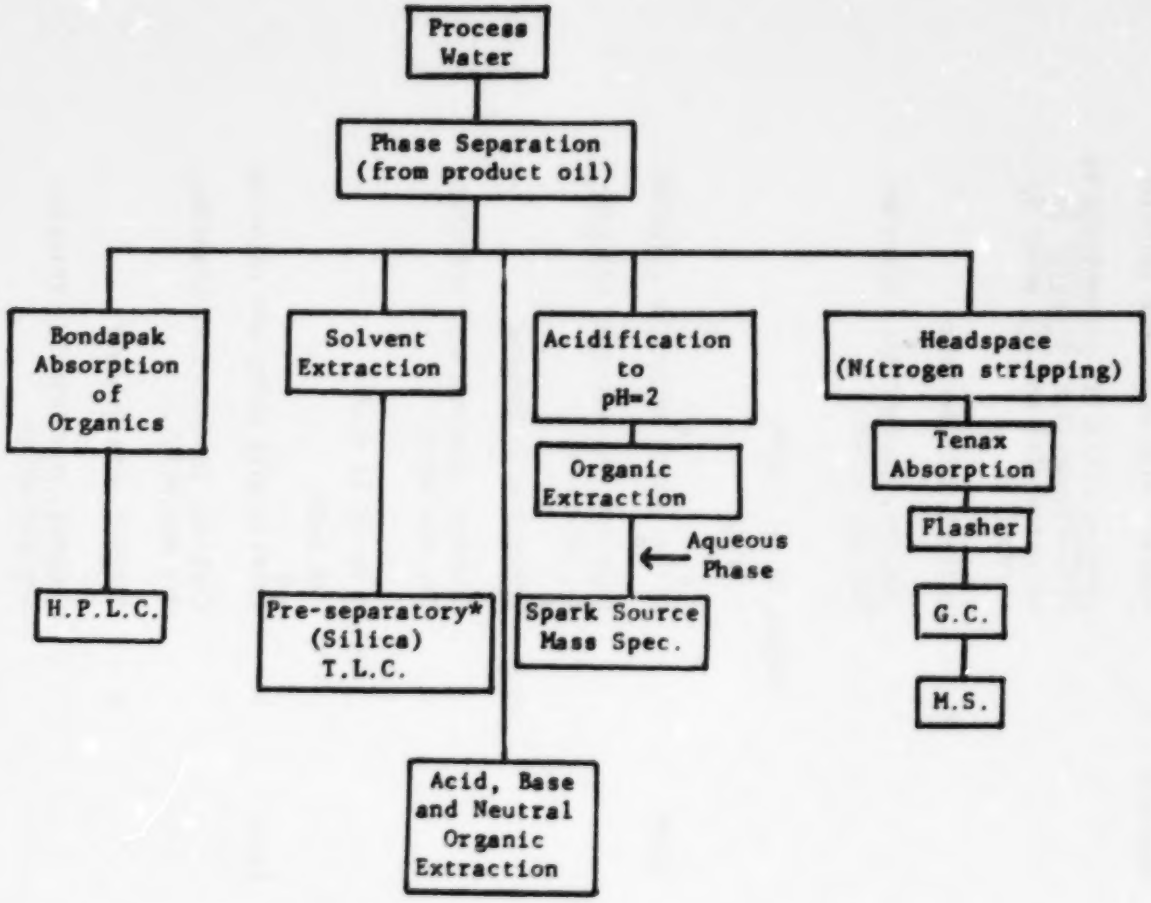
The analytical schemes for gaseous, water, and solid samples are illustrated in Figures B1 through B-6.

Detailed descriptions of these analytical methods are continued in a separate report, Volume II.



* NOT USED DUE TO THE PRESENCE OF AEROSOL

Figure B-1. Analytical schematic for recycle gas stream.



*See T.L.C. Analytical Scheme Figure

Figure B-2. Separation and analysis scheme for water samples.

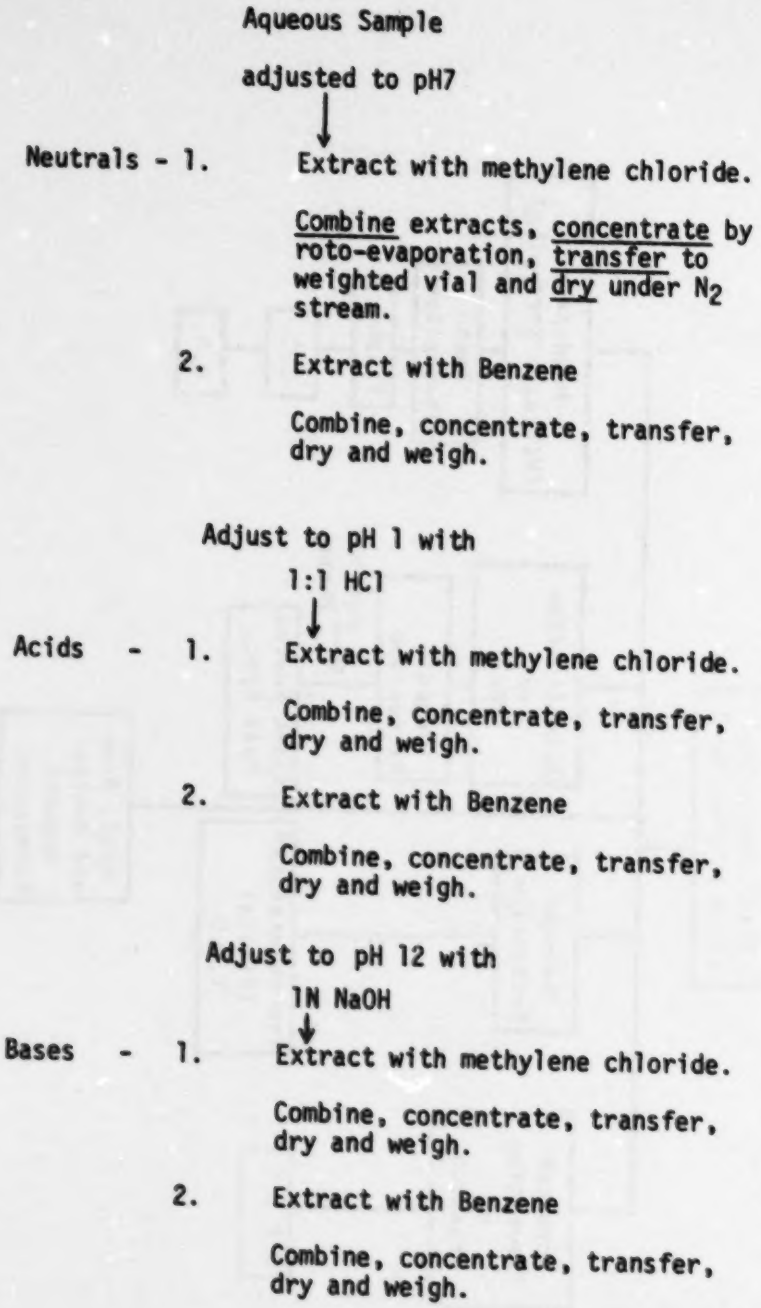

Aqueous Sample
adjusted to pH7
Neutrals - 1.
Extract with methylene chloride.
Combine extracts, concentrate by roto-evaporation, transfer to weighted vial and dry under N_2 stream.
2.
Extract with Benzene
Combine, concentrate, transfer, dry and weigh.
Adjust to pH 1 with
1:1 HCl
Acids - 1.
Extract with methylene chloride.
Combine, concentrate, transfer, dry and weigh.
2.
Extract with Benzene
Combine, concentrate, transfer, dry and weigh.
Adjust to pH 12 with
1N NaOH
Bases - 1.
Extract with methylene chloride.
Combine, concentrate, transfer, dry and weigh.
2.
Extract with Benzene
Combine, concentrate, transfer, dry and weigh.

Figure B-3. Flow diagram for extraction of organics from aqueous phase of recycled gas condensates.

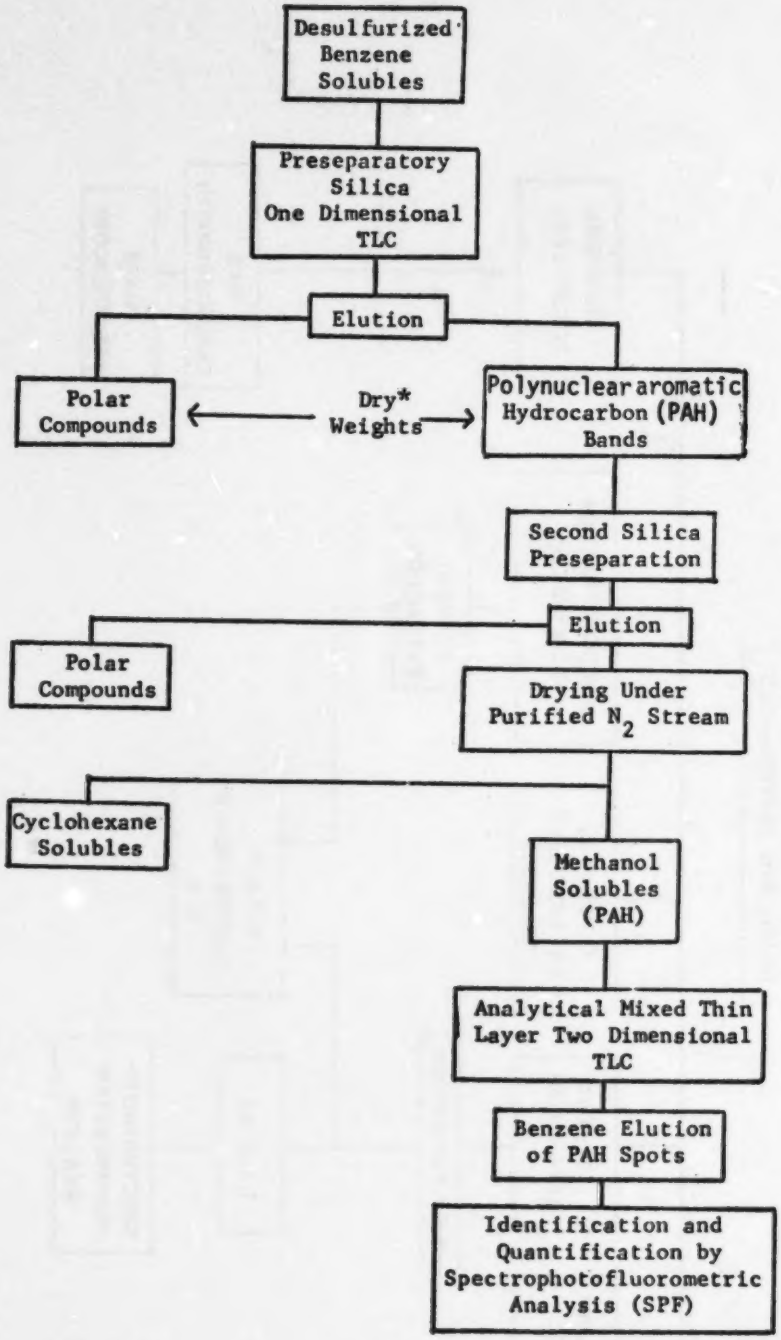
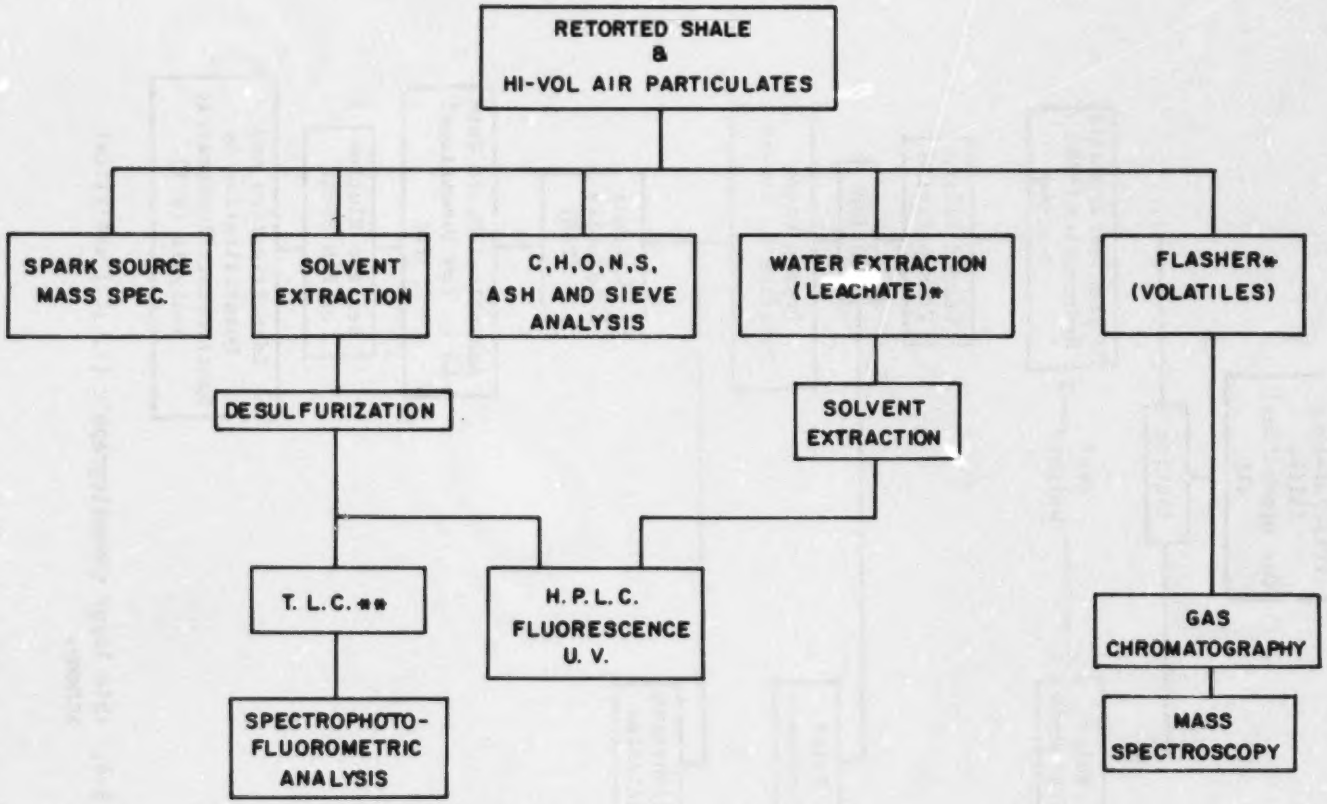


Figure B-4. Thin layer chromatographic (T.L.C.) analytical scheme.

*Denotes point at which reported preseparatory dry weights were taken.



* NOT PERFORMED ON AIR PARTICULATES.

** SEE T.L.C. ANALYTICAL SCHEME FIGURE

Figure B-5. Analysis schematic for retorted shale and high-vol air particulates.

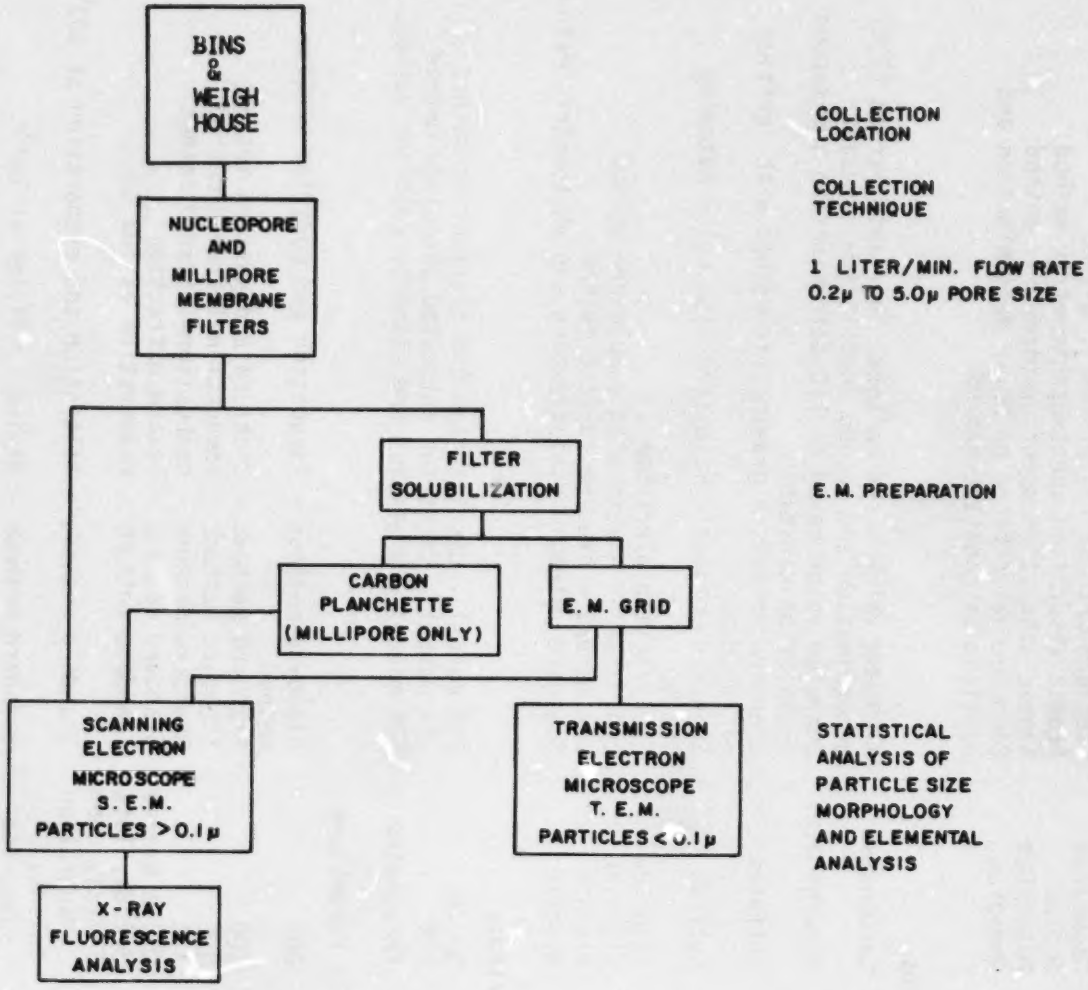

BINS & WEIGH HOUSE
NUCLEOPORE AND MILLIPORE MEMBRANE FILTERS
FILTER SOLUBILIZATION
CARBON PLANCHETTE (MILLIPORE ONLY)
E. M. GRID
SCANNING ELECTRON MICROSCOPE S. E. M. PARTICLES >0.1μ
TRANSMISSION ELECTRON MICROSCOPE T. E. M. PARTICLES <0.1μ
X-RAY FLUORESCENCE ANALYSIS
COLLECTION LOCATION
COLLECTION TECHNIQUE
1 LITER/MIN. FLOW RATE 0.2μ TO 5.0μ PORE SIZE
E. M. PREPARATION
STATISTICAL ANALYSIS OF PARTICLE SIZE MORPHOLOGY AND ELEMENTAL ANALYSIS

Figure B-6. Collection & analysis schematic for low-vol air particulates

WATER ANALYSIS METHODOLOGY FOR INORGANICS AND GROSS PARAMETERS

Parameter	Method of Analysis
Cations	
Calcium	Standard methods* - permanganate titrimetric method
Magnesium	Standard methods - gravimetric method
Sodium	Atomic absorption spectrophotometric method
Potassium	Atomic absorption spectrophotometric method
Ammonium	Computed value based on NH_3-N determination and equilibrium constant and pH
Anions	
Carbonates	Computed value based on total inorganic carbon (TIC) determination and second equilibrium constant
Bicarbonates	Computed value based on TIC determination and second equilibrium constant
Sulfates	Standard methods - gravimetric method with ignition of residues
Sulfide	Standard methods - methylene blue color matching method
Chloride	Specific ion electrode
Fluoride	EPA manual** - automated complexone method
Nitrate	EPA manual - brucine sulfate method
Nitrite	Standard method - diazotization and photometric method
Nutrients	
NH_3-N	EPA manual - distillation and titrimetric method
TKN	EPA manual - digestion automated phenolate method
Phosphates	EPA manual - digestion and stannous chloride method
Gross Parameters	
BOD	Standard methods - incubation and modified winkler method
COD	Standard methods - dichromate digestion method
TOC	Standard methods - combustion-infrared method
TIC	Standard methods - combustion-infrared method
Oil & Grease	Standard methods - hexane extraction
Solids, Total	Standard methods - evaporation at 103°C
Solids, upon evaporation	Standard methods - filtration and evaporation at 103°C
Solids, suspended	Standard methods - drying of filter at 103°C
Total Alkalinity	Standard methods - titrimetric
Hardness	Standard methods - calculated value based on Ca and Mg conc.
Phenols	Standard method - distillation and photometric
pH	pH meter - instrumental method

*Standard Methods for the Examination of Water and Wastewater, American Public Health Assn., Washington, D.C.: 13th Ed., 1971.
**Methods for Chemical Analysis of Water and Waste, EPA 625-6-74-003.

Theoretical Computation of Concentrations of Bicarbonates (HCO_3^-), Carbonates ($CO_3^=$) and Ammonium Ions for Condensate Samples

Bicarbonates and Carbonates

$K_2 = 4.7 \times 10^{-11}$

Total Inorganic Carbon (TIC) = 9800 mg/l = 817 millimoles

Assume 0.1M ionic strength activity coefficient $\gamma CO_3^= = 0.38$

$\gamma HCO_3^- = 0.77$

$$K_2 = \frac{(H+)(CO_3^=)}{(HCO_3^-)} \quad \frac{\gamma H+ \ \gamma CO_3^=}{\gamma HCO_3^-} = \left[\frac{(CO_3^=)}{(HCO_3^-)} \ \alpha H+\right] \frac{\gamma CO_3^=}{\gamma HCO_3^-}$$

$$K_2^1 = \text{conditional constant} = K_2 \frac{\gamma HCO_3^-}{\gamma CO_3^=} = 4.7 \times 10^{-11} \times \frac{0.77}{0.38} =$$

$$= 9.5 \times 10^{-11}$$

$$C_T = C_{H_2CO_3} + C_{HCO_3^-} + C_{CO_3^=}$$

Since pH of wastewaters are around 9, the only significant ions are HCO_3^- and $CO_3^=$

$$\therefore C_T \simeq (HCO_3^-) + (CO_3^=)$$

Let $x = (HCO_3^-)$

$$\therefore \frac{K_2^1}{(H+)} = \frac{K_2^1}{\alpha H+} = \frac{(CO_3^=)}{(HCO_3^-)} = \frac{C_T - x}{x}$$

(i) for pilot plant (at pH = 9.8, $\alpha H+ = 1.58 \times 10^{-10}$

$$\frac{9.5 \times 10^{-11}}{1.58 \times 10^{-10}} = \frac{817 - x}{x}$$

$$\therefore x = \frac{817}{1.594} = 512 \text{ Millimoles of } HCO_3 \text{ or } 31{,}265 \text{ mg/l}$$

$(CO_3^=) = 817 - 512 = 305$ Millimoles or 30,500 mg/l

(ii) for semi-works plant (at pH - 9.5, $\alpha H^+ = 3.16 \times 10^{-10}$)

C_T = 1600 mg/l = 133.3 Millimoles

$$\frac{9.5 \times 10^{-11}}{3.16 \times 10^{-10}} = \frac{133.3 - x}{x}$$

$x = [HCO_3^-] = \frac{133.3}{1.3}$ = 103 Millimoles or 6280 mg/l

$[CO_3^=]$ = 30.3 Millimoles or 3030 mg/l

Ammonium Ions

$K_{NH_3} = 1.8 \times 10^{-5}$

Total Ammonia = C_{T_1} = 19,400 mg/l = 1141 Millimoles

C_{T_2} = 29,600 mg/l = 1741 Millimoles

Assume 0.1M ionic strength activity coefficient $\gamma NH_3 = 1$

$\gamma NH_4^+ = 0.75$

$$K_{NH_3} + \frac{(NH^+)}{(NH_3)} \alpha OH^- \frac{\gamma NH_4^+}{\gamma NH_3}$$

$$K^1_{NH_3} = \left[\frac{(NH_4^+)}{(NH_3)}\right] \alpha OH^- \frac{\gamma NH_3}{\gamma NH_4^+} = K_{NH_3} \frac{\gamma NH_3}{\gamma NH_4^+} = \frac{1.8 \times 10^{-5} \times 1}{0.75}$$

$= 2.4 \times 10^{-5}$

$C_T = (NH_3) + (NH_4^+)$

$$\frac{K^1_{NH_3}}{\alpha ON^-} = \frac{(NH_4^+)}{(NH_3)} = \frac{C_T - x}{x} \quad \text{where } x = (NH_3)$$

(i) for pilot plant (at pH = 9.8, $OH^- = 6.31 \times 10^{-5}$

$$\therefore \frac{2.4 \times 10^{-5}}{6.31 \times 10^{-5}} = \frac{1141 - x}{x}$$

$\therefore x = \frac{1141}{1.38}$ = 827 Millimoles or 14,060 mg/l = (NH_3)

(NH_4^+) = 314 Millimoles or 5650 mg/l

(ii) for semi-works plant (at pH 9.5, $\alpha OH^- = 3.16 \times 10^{-5}$

$$\therefore \frac{2.4 \times 10^{-5}}{3.16 \times 10^{-5}} = \frac{1741 - x}{x}$$

$$\therefore x = \frac{1741}{1.76} = 989 \text{ Millimoles or } 16{,}800 \text{ mg/l } NH_3$$

(NH_4^+) = 752 Millimoles NH_4^+ or 13,540 mg/l

REPRESENTATIVE INSTRUMENT TRACES

Figure B7 - HPLC Chromatogram of Pilot Plant Cold Condensate

Figure B8 - Fluorescent Spectrum of BaP Spot for Two Dimension TLC (refer to Figure 10)

Figure B9 - X-ray Fluorescence Spectrum of Raw Shale Particulate

Figure B10 - Scanning Electron Micrograph of Air Particulate

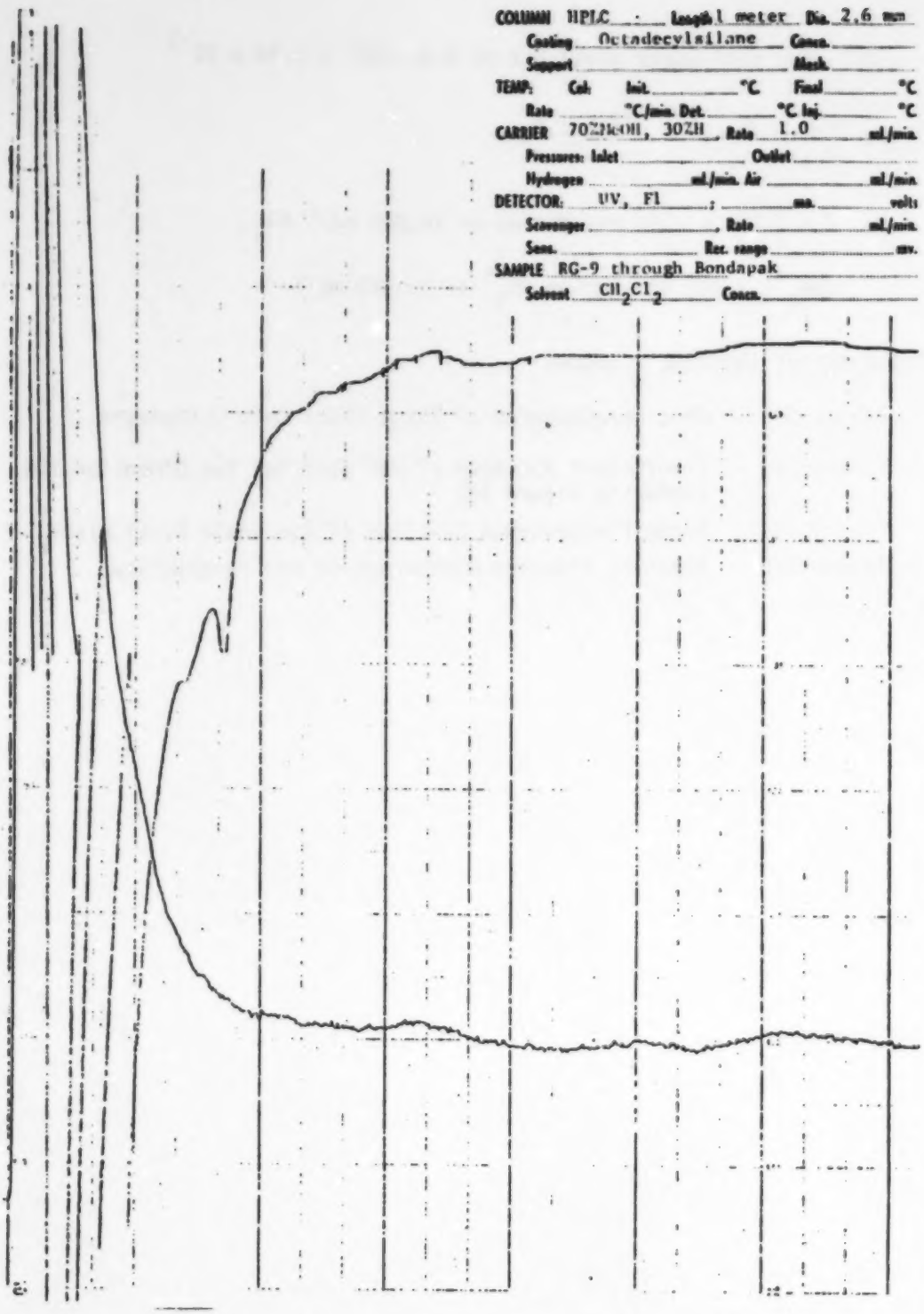

COLUMN HPLC . Length meter Dia. 2.6 mm
Coating Octadecylsilane Conc.
Support Mesh
TEMP: Col: Init. °C Final °C
Rate °C/min. Det. °C Inj. °C
CARRIER 70%MeOH, 30%H Rate 1.0 ml/min.
Pressures: Inlet Outlet
Hydrogen ml/min. Air ml/min.
DETECTOR: UV, Fl ; ma. volts
Scavenger , Rate ml/min.
Sens. Rec. range mv.
SAMPLE RG-9 through Bondapak
Solvent CH_2Cl_2 Conc.

Figure B-7. HPLC chromatogram of bondapak adsorbed material from pilot plant recycled gas condensate (cold) sample RG-9.

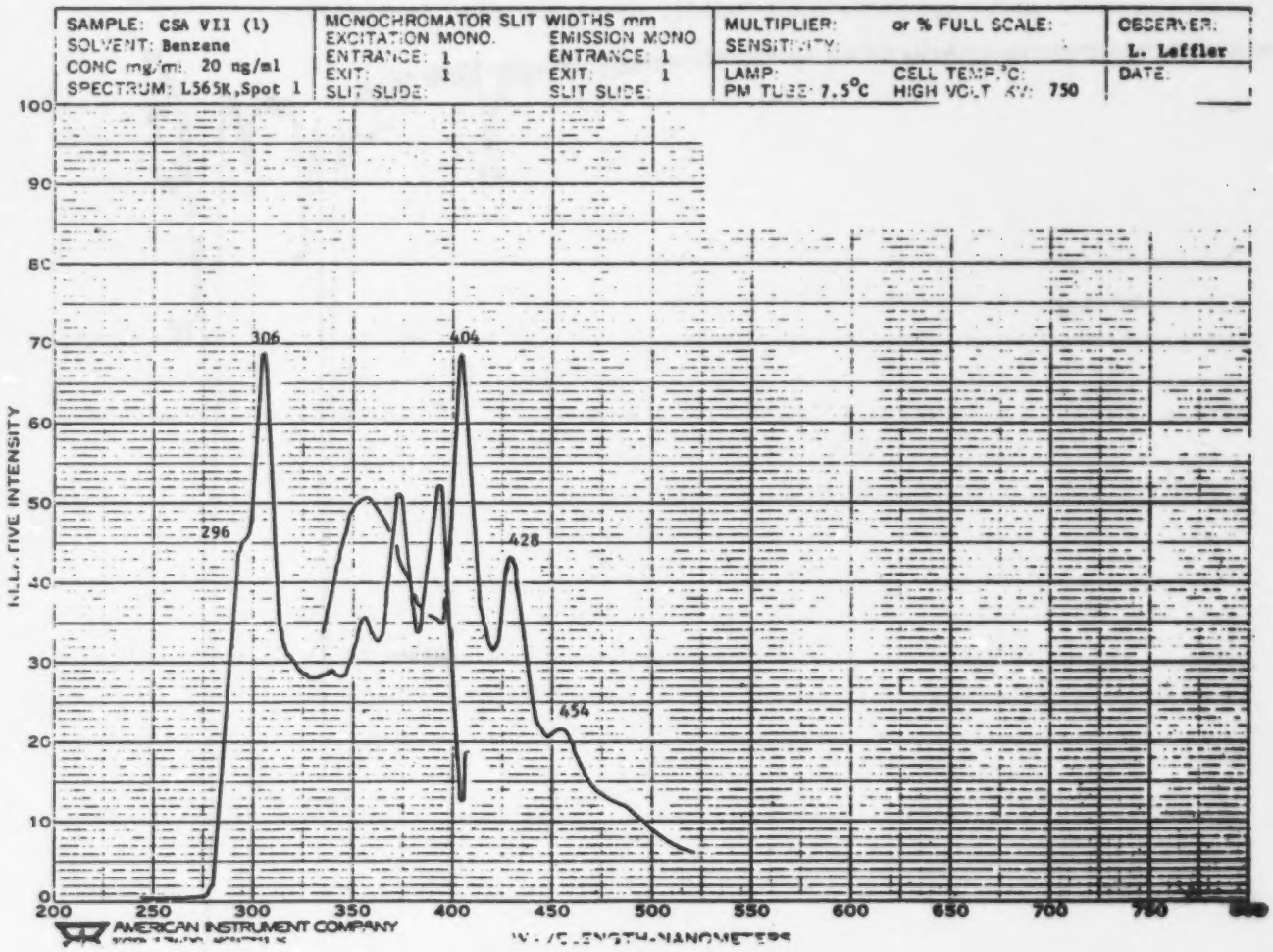


Figure B-8. Fluorescent spectrum of BaP spot from a two dimensional mixed thin layer chromatogram - L565k.

EXCITATION WAVELENGTH - 300 nm
EMISSION WAVELENGTH - 404 nm

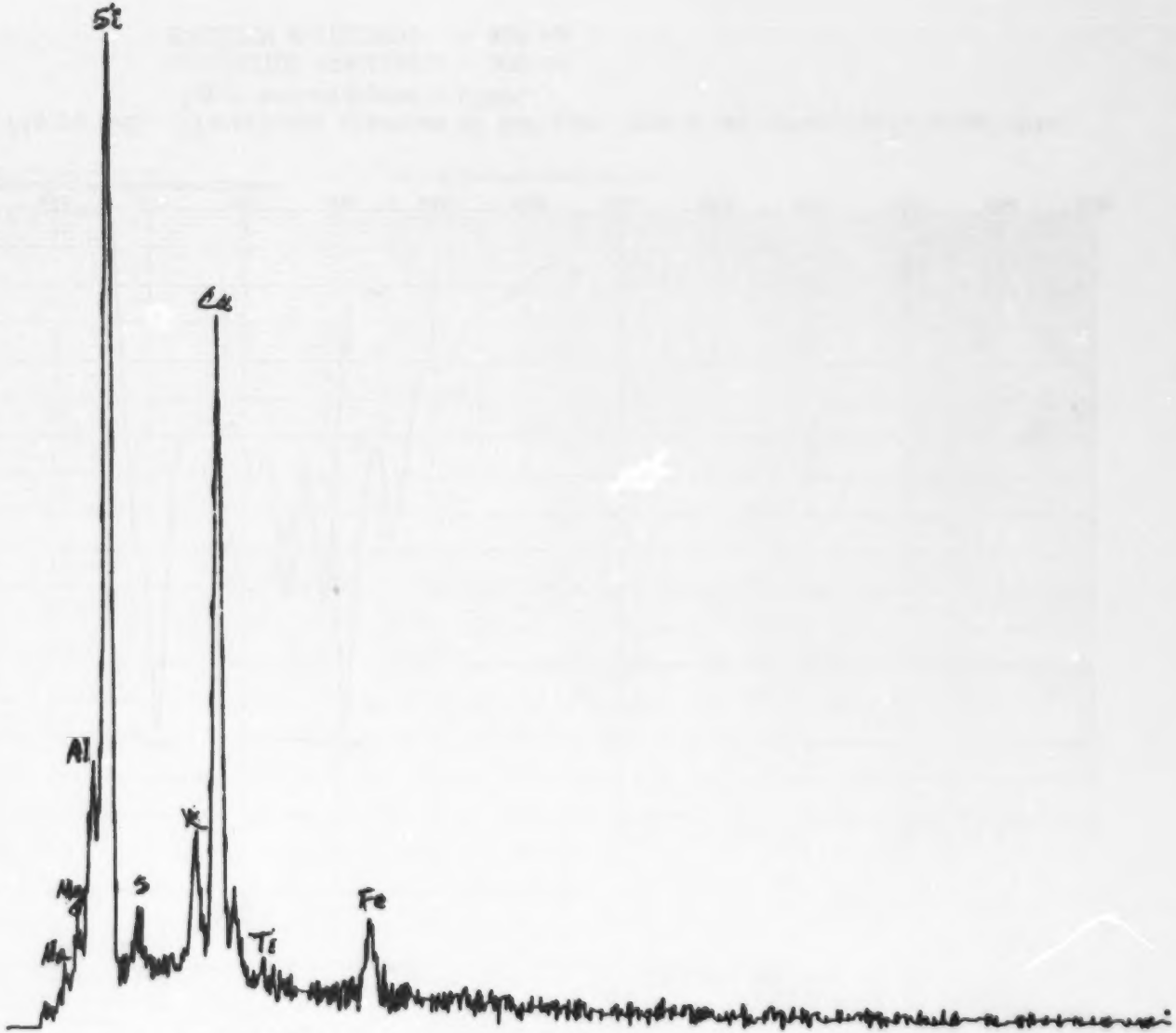


Figure B-9. Typical x-ray fluorescence spectrum of an unretorted shale air particulate particle.

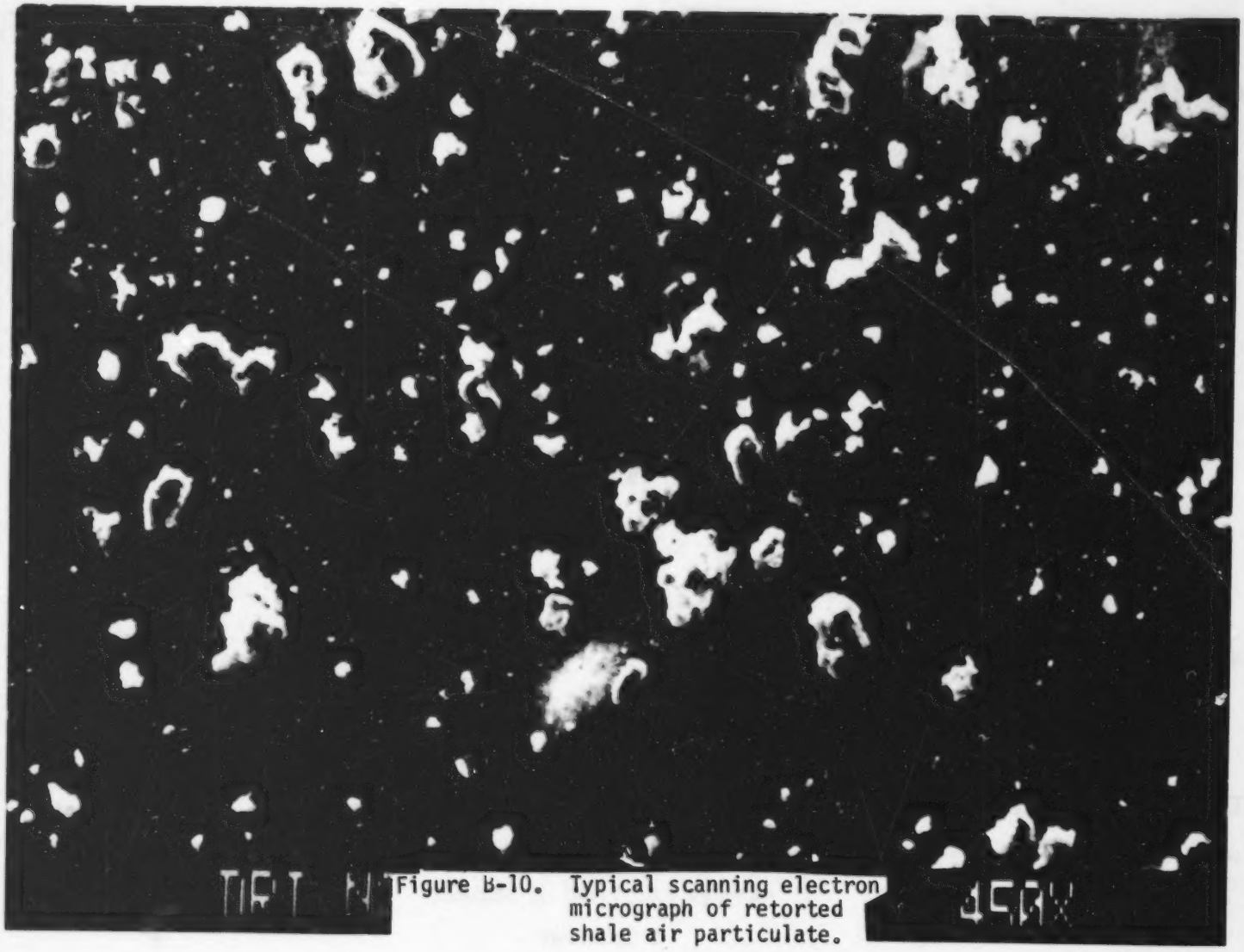


Figure B-10. Typical scanning electron micrograph of retorted shale air particulate.

APPENDIX C

SUMMARY OF COLLECTED SAMPLES

Sample Type	Sampling Location	Date	Time	Test to be Performed	Analysis
A. Gas Sampling Trains					
Absorption Solution	Semi works recycle gas (suction side)	3-15-76	12pm,4pm	Kjeldahl distillation, titration	NH_3
Absorption Solution	Pilot plant recycle gas (suction side)	3-11-76 3-10-76	9am,11am 2pm	Colorimetric	Arsine
"	"	3-12-76	9am,2pm	Kjeldahl distillation, titration	
"	"	3-12-76	4pm		HCN
"	"	3-12-76	4pm		CS_2
"	"	3-11-76	2pm,4pm	Kjeldahl distillation, titration	COS
					NH_3
Absorption Solution	Semi works recycle gas (suction side)	3-15-76	5-5:30pm		NO_x
"	"	3-14-76	3pm,4:30pm	Titration	SO_2
Absorption Solution	Pilot plant recycle gas (suction side)	3-9-76	1:30pm-3:45pm	Colorimetric	NO
"	"	3-9-76	2pm,3pm	Barium perchlorate titration	SO_2
"	"	3-10-76	9am,11am	Colorimetric	H_2S
B. Cascade Impaction Plates					
Impaction Plates	Primary Crusher	3-17-76	2pm	Gravimetric	

Sample Number	Sample Type	Location	Date	Time	Notes/Types of Analysis
C. High Vol Filters					
18	High Vol Filter	Primary crusher building S.W. of crusher	3-15-76	0815 to 0830 (3-16)	*
2	"	"	3-16-76	0830-1635	*
22	"	"	3-16-76	1635 to 0915 (3-17)	*
27	"	"	3-17-76	0915-1530	*
32	"	"	3-17-76	1535 to 0830 (3-18)	*
17	"	Secondary crusher bldg. on balcony at south end of bldg.	3-15-76	0810 to 0835 (3-16)	Organic extraction & elemental analysis
12	"	"	3-16-76	0835-1645	Organic extraction
23	"	"	3-16-76	1645 to 0920 (3-17)	*
28	"	"	3-17-76	0920-1535	Organic extraction
33	"	"	3-17-76	1540 to 0835 (3-18)	Sample ruined in handling
16	"	Bins and weigh house lower level on output end	3-15-76	0805 to 0845 (3-16)	Organic extraction and x-ray fluorescence analysis
13	"	"	3-16-76	1000-1645	"
24	"	"	3-16-76	1645 to 0930 (3-17)	Organic extraction
29	"	"	3-17-76	0930-1530	"
34	"	"	3-17-76	1545 to 0840 (3-18)	"

Sample Number	Sample Type	Location	Date	Time	Notes/Type of Analysis
D. Low Vol Filters					
M2	5 Millipore Filter, 1 min	Bins and weigh house	3-15-76	1000	*
M4	5 Millipore Filter, 2 min.	"	3-15-76	1005	*
M7	5 Millipore Filter, 5 min.	"	"	1010	*
M5	5 Millipore Filter, 10 min.	"	"	1025	X-ray fluorescence analysis
N4	0.2 Nucleopore Filter, 5 min.	"	"	1400	*
N5	0.2 Nucleopore	"	"	1410	Used for scanning electron microscope, X-ray fluorescence and transission electron microscope analysis
E. Bulk Samples					
CSA VII (A)	Retorted Shale Bulk Sample 2 cans	Next to dump chute out of pilot plant before screen conveyor (direct mode)	3-9-76	1000	Combined with CSA VII (B) for organic extraction, inorganic (leachate) extraction, SSMS and elemental analysis
CSA VII (B)	"	"	3-12-76	1000	See CSA VII (A) above. Volatiles analysis - GC-MS
Oil (Process Water)	Product Oil 10 gal.	Semi-works (indirect mode)	3-15-76	1500	Used for phase separation of process water from oil. Trace inorganics by spark source mass spec. HPLC GC-MS

Sample Number	Sample Type	Location	Date	Time	Notes/Type of Analysis
F. Recycle Gas Stream Absorption Samples					
MSA 1 2 3 4 5 6	MSA Charcoal Tube Absorption 1 min.	Pilot plant recycle gas	3-10-76	1300	*
MSA 15 16 17 18	" 5 min.	"	3-10-76	1315 to 1345	MSA 15 GC-MS " 16 "
MSA 7 8 9 10	" 1 min.	Pilot plant recycle gas blower output using Teflon condenser	3-10-76	1345	MSA 7 GC-MS
MSA 11 12 13 14	" 5 min.	"	3-10-76	1400 to 1430	MSA 11 GC-MS
B1	Gastec Tube CO Type 1H	Pilot plant recycle gas blower output	3-10-76	1430	Direct indicating gas analysis tubes used for backup and/or verification of other procedures
B2	CO_2 Type 2H				
B3	HCN Type 12H	Pilot plant recycle gas blower output	3-10-76	1430	Direct indicating gas analysis tubes used for backup and/or verification of other analytical procedures

Sample Number	Sample Type	Location	Date	Time	Notes/Type of Analysis
F. Recycle Gas Stream Absorption Samples					
B4	H_2S Type 4H	Pilot plant recycle gas blower output	3-10-76	1445	Direct indicating gas analysis tubes used for backup and/or verification of other analytical procedures
B5	$NO-NO_2$ Type 10	"	"	1445	"
B6	NH_3 Type 3M	"	"	1445	"
B7	SO_2 Type 5L	"	"	1445	"
Bendix 17 31 32 34	Bendix Charcoal Flasher Tube 1 min. ea.	"	"	1515	*
Bendix 4 10 14 21	"	"	"	1530 to 1555	Bendix 4 - GC-MS
T9 T6 T20 T4	Tenax Absorption Tubes 1 min. ea.	"	"	1600	*
T7 T15 T19 T18	" 5 min. ea.	"	"	1615 to 1640	*

Sample Number	Sample Type	Location	Date	Time	Notes/Type of Analysis
G. Gas Bottle Samples					
G1 G2 G3	250 ml gas bottle (triplicate)	Pilot plant recycle gas (output side of blower)	3-10-76	1730	G1-GC-MS
H. Recycle Gas Condensate Samples					
RG1	Recycle gas cold condensate	Pilot plant (direct mode) recycle gas blower output	3-10-76	1000 to 1500	Benzene preserved in field; sent to TRW for analysis
RG2	"	"	3-11-76	0800 to 1400	TC - TOC analysis
RG3	"	"	3-10-76	1700 to 0800 (3-11)	Acidified to pH2 in field; organics extracted used for inorganic trace analysis by spark source mass spectroscopy.
RG4	"	"	3-15-76	0800 to 1200	TC - TOC analysis
RG9	"	"	3-16-76	0800 to 1200	GC-MS, HPLC and TC - TOC analysis.
RG5	Recycle gas condensate (hot)	Semi-works recycle gas condensate tank	3-15-76	1000	Benzene extracted in field. Acidified in field.

*Indicates sample not used for analysis.

Note: Within any given time slot, gas stream absorption samples are listed according to the order in which they were collected.
SSMS - Spark Source Mass Spectroscopy
GC-MS - Gas Chromatography Couples Mass Spectroscopy
HPLC - High Pressure Liquid Chromatography
TLC - Thin Layer Chromatography
GPC - Gel-Permeation Chromatography

Sample Number	Sample Type	Location	Date	Time	Notes/Type of Analysis
	Water sample	Semi-Works recycle gas condensate (hot)	3-14-76	0800 to 1800	All inorganic and non-specific
	Water sample	Pilot plant recycle gas (cold)	3-11-76	0800 to 1800	All inorganic and non-specific